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DETERMINATION OF THE FEASIBILITY OF THE LONG-RANGE TRANSPORT OF OZONE OR OZONE PRECURSORS

D. L. Blumenthal, et al

Meteorology Research Incorporated

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DETERMINATION OF THE FEASIBILITY OF THE LONG-RANGE TRANSPORT OF OZONE OR OZONE PRECURSORS

by

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November 1974

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16. ABSTRACT

In the last few years, Meteorology Research, Inc. (MRI) has conducted numerous studies of the three-dimensional distribution and transport of air pollutants. From the extensive data base collected, the export of ozone or its precursors from the Los Angeles and Denver metropolitan areas was documented. Analysis of the July 25, 1973 smog episode in the Los Angeles Air Basin indicated that ozone was being exported from the western, heavily urbanized, portion of the basin at rates exceeding 100 metric tons per hour during much of the afternoon. High ozone concentrations confined to the surface mixing layer in the relatively remote mountain and desert areas east and northeast of Los Angeles were documented and traced back to their probable source in the Los Angeles Air Basin. The stability of ozone at elevated concentrations was documented by observations in the Los Angeles Air Basin during July 26-27, 1973 which revealed a layer of aged polluted air above the surface mixing layer, with ozone concentrations which remained undiminished at 0.12 - 0.13 ppm throughout the night. Standard diffusion estimates based on one episode indicated that, over flat terrain in the absence of scavenging mechanisms, an ozone source the size of the Los Angeles metropolitan area could cause ozone concentrations to exceed the Federal standard of 0.08 ppm at locations as far away as 260 km. From the data studied, it was concluded that urban sources can have a substantial effect on ozone concentrations in downwind areas, and that this effect can carry over more than one day.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone Transport Meteorology Photochemical Measurements Airborne		

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I. INTRODUCTION

Recent studies (Kelly, 1970; Ripperton, 1974) have indicated the presence of ozone in rural areas at levels which exceed the Federal Ambient Air Standard of 0.08 ppm. The source of this ozone remains in doubt, and speculation as to its origin ranges from injection into the troposphere from the stratosphere to long-range transport of ozone from urban areas. The Environmental Protection Agency (EPA) is interested in resolving the question of the source of the high levels of ozone because of the implications for control strategy and standards setting. This study attempts to show that at least in some instances, high levels of ozone in rural areas can be due to transport from urban sources as far away as 100 km or more.

In the last few years, Meteorology Research, Inc. (MRI), has conducted numerous and extensive three-dimensional air pollutant studies using an airborne sampling system. Vertical, as well as horizontal, data have been obtained for O_3, CO, NO_x, SO_2, condensation nuclei, scattering coefficient (b_{scat}), temperature, turbulence, and relative humidity. Detailed meteorological data were also obtained during most of the programs. These studies have been performed in places such as Los Angeles, St. Louis, Denver, the San Joaquin Valley, Alaska, New Mexico, and Oregon with the most extensive data package having been obtained for the Los Angeles (L.A.) Basin and its surroundings.

The MRI data generally show a background ozone level of 0.04 ppm or slightly lower in clean air. In all the MRI studies, even in rural areas, when the O_3 level exceeded about 0.05 ppm, a distinct surface-based mixing layer or layer aloft was definable. Within this layer other indications of pollutants such as elevated levels of condensation nuclei or light scattering coefficient (b_{scat}) were also present. Outside of the layer, the ozone concentration, as well as those of other pollutants dropped to clean air values. In general, the polluted layers aloft were easily explainable in terms of transport aloft from the surface by normal meteorological means. This indicates that, at least for the cases studied by MRI, the ozone exceeding the background level was of surface origin.

The object of the present study is to determine the feasibility of transport of ozone or its precursors from urban source areas to rural receptor areas far downwind. This is done by the careful study of selected pollutant episodes in which various phases of the transport process can be well documented. While the case histories selected are considered

typical of pollutant episodes, no attempt is made to relate them to annual statistics. The data used in this study were obtained under various contracts with the California Air Resources Board and the Environmental Protection Agency.

To begin with, the export of ozone or its precursors from Los Angeles and Denver is documented. Relatively rural areas such as Redlands, downwind of Los Angeles, and Standley Lake, downwind of Denver, are considered as receptor areas, and several days when high ozone concentrations were observed during the afternoon at these locations are taken as examples. Using the extensive winds aloft and surface wind data, the ozone-laden air masses arriving at these locations are traced back for several hours to sources over industrialized and heavily populated urban areas. Some of the receptor areas themselves have sources of ozone precursors which may affect ozone concentrations even further downwind. For the episodes studied, however, analysis of the pollutant burdens of the air masses involved indicates that most of the ozone precursors present at the receptor sites were picked up over the urban areas upwind, and that most of the ozone measured was either exported directly from the urban areas or formed en route as the air mass aged in the absence of extensive new emissions.

The case studies described above present a strong argument to document the export of ozone or its precursors from urban areas for three different days. In order to show the potential for multiday transport, evidence of the overnight stability of ozone at elevated concentrations (more than 0.10 ppm) in aged polluted air is presented, and the existence of ozone in the rain is documented.

Examples are also presented of high ozone concentrations confined to the surface mixing layer in the relatively remote mountain and desert areas east and northeast of Los Angeles. The ozone-laden air arriving at these locations is traced back to the probable source of the ozone precursors in the Los Angeles Air Basin.

The bulk of the evidence indicates that urban areas can be a source of high concentrations of ozone or ozone precursors found in at least a few specific rural areas. Based on a specific episode, an estimate of the potential effect of a city the size of Los Angeles on downwind ozone concentrations is made. Using standard diffusion estimates, it is shown that an urban source of this size could cause the ambient air ozone standard of 0.08 ppm to be exceeded as far as 260 km downwind of the source.

II. EXPORT OF OZONE AND OZONE PRECURSORS FROM URBAN AREAS

A. Los Angeles Basin

1. Background

The Los Angeles air basin can be divided into two sub-basins separated roughly by the Chino Hills, as shown in Fig. II-1. The western basin encompasses the heavily urbanized portions of Los Angeles and Orange Counties, while the eastern basin lies in more rural San Bernardino and Riverside Counties. As indicated in Table II-1, the estimated daily emissions of primary pollutants in the eastern basin are much lower than they are in the western basin.

As shown in Fig. II-2 (from Smith et al., 1972), afternoon surface winds during the summer months are predominantly westerly, under the influence of the sea breeze. It is clear from the pattern of the surface winds that air is transported from the western basin into the eastern basin during a typical summer afternoon. This has been verified by recent tracer studies conducted for the California Air Resources Board. On seven summer and early fall days in 1972 and 1973, Metronics Associates, Inc., released color coded fluorescent particles in the vicinity of Los Angeles (CAP), Torrance (TOA), and Santa Ana (SNA) (Vaughan and Stankunas, 1973, 1974). On most of these days, particles from Los Angeles and Torrance were picked up in Redlands (RED) by 1600 PDT. An example is shown in Fig. II-3.

Although transport from the western basin to the eastern basin is now well documented, the magnitude of its effects on pollutant concentrations downwind is difficult to establish without knowledge of their three-dimensional distribution. As cooler marine air from the coast is carried inland it is warmed by the ground, and the mixing layer deepens. The resulting dilution of pollutants by clean air as they mix through a deepening layer and other meteorological effects tend to obscure the effects of transport on surface concentrations. This study uses data obtained during a three-dimensional pollutant mapping program to gain a better understanding of the transport phenomena at work in the L.A. Basin and to obtain an estimate of the effects of pollutants exported from the western basin on the concentrations observed in the eastern basin.

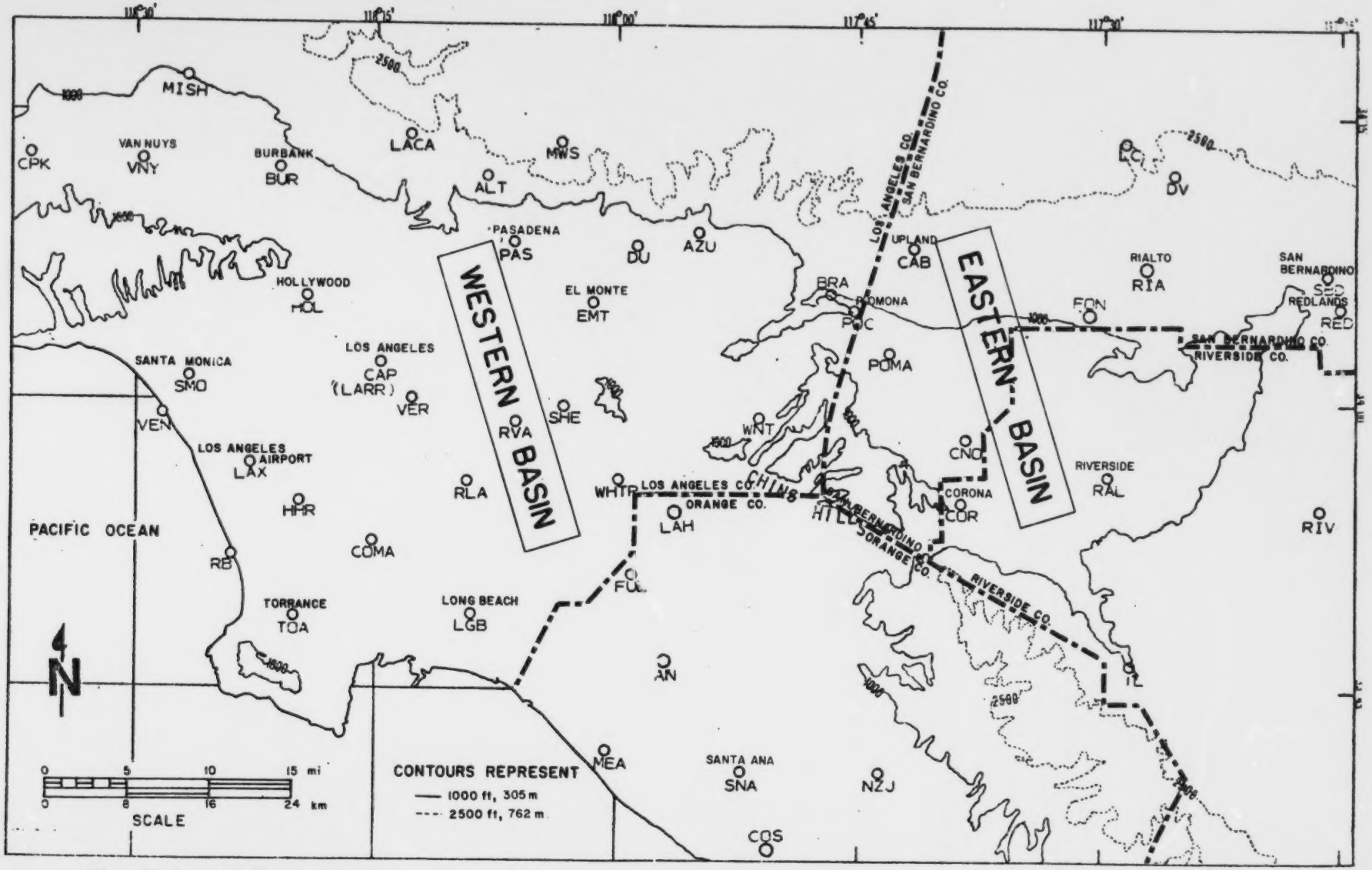


Fig. II-1. MAP OF THE LOS ANGELES AIR BASIN SHOWING EAST AND WEST BASINS
(Circles are locations of weather or air pollution monitoring stations or airports (spiral points).)

Table II-1

ESTIMATED AVERAGE DAILY EMISSIONS IN 1970 IN METRIC TONS PER DAY

	Los Angeles County* and Orange County	Riverside County* and San Bernardino County*
RHC	1395	135
NO_x	1210	120
CO	8820	935
SO_2	240	40

Figures are from the State of California Implementation Plan for Achieving and Maintaining the National Ambient Air Quality Standards, California Air Resources Board, 1972.

*Only that portion of the county lying within the South Coast Air Basin is included.

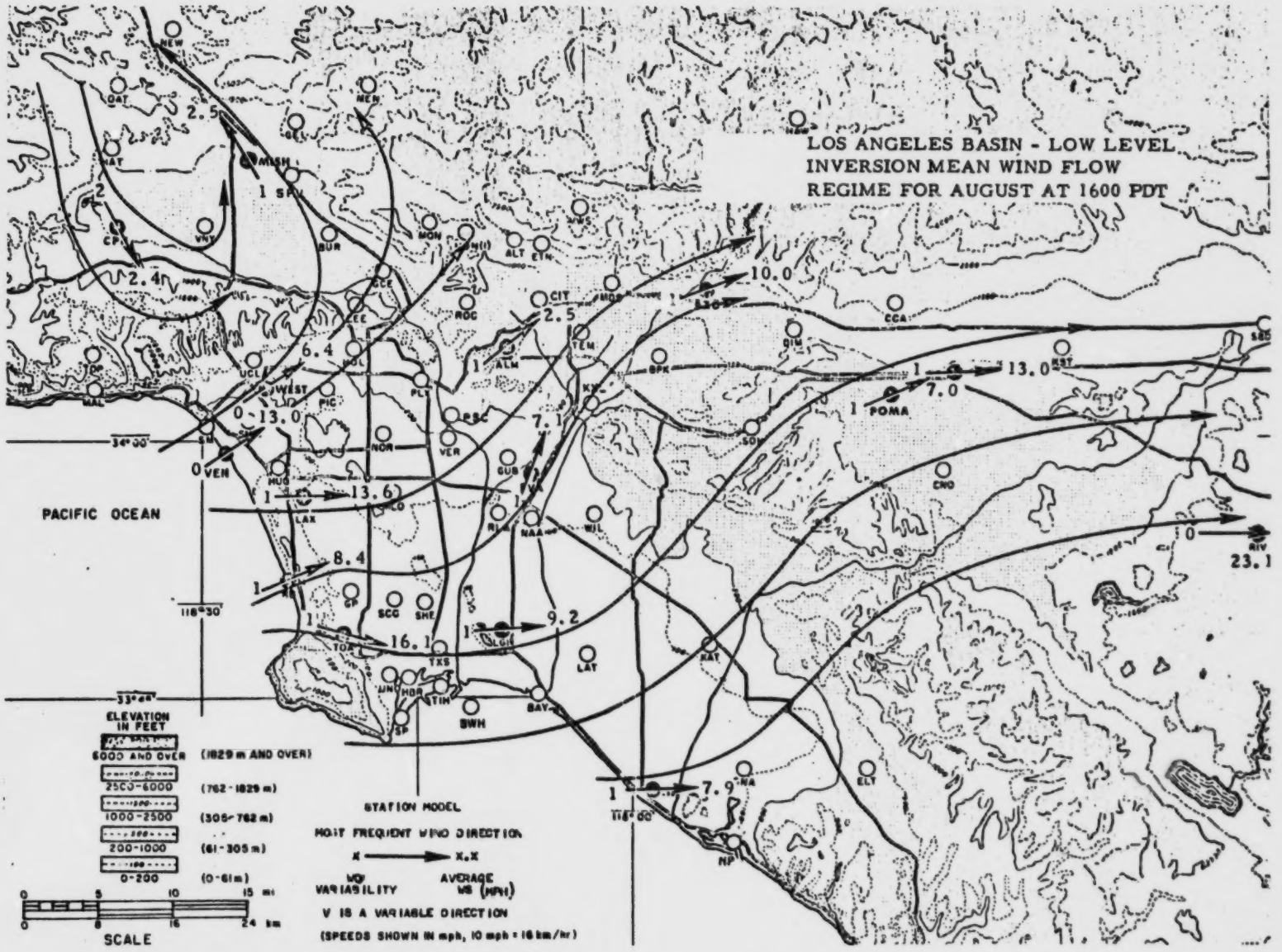


Fig. II-2. LOS ANGELES BASIN MEAN WIND FLOW FOR DAYS WITH LOW LEVEL INVERSIONS DURING AUGUST 1970 AT 1600 PDT

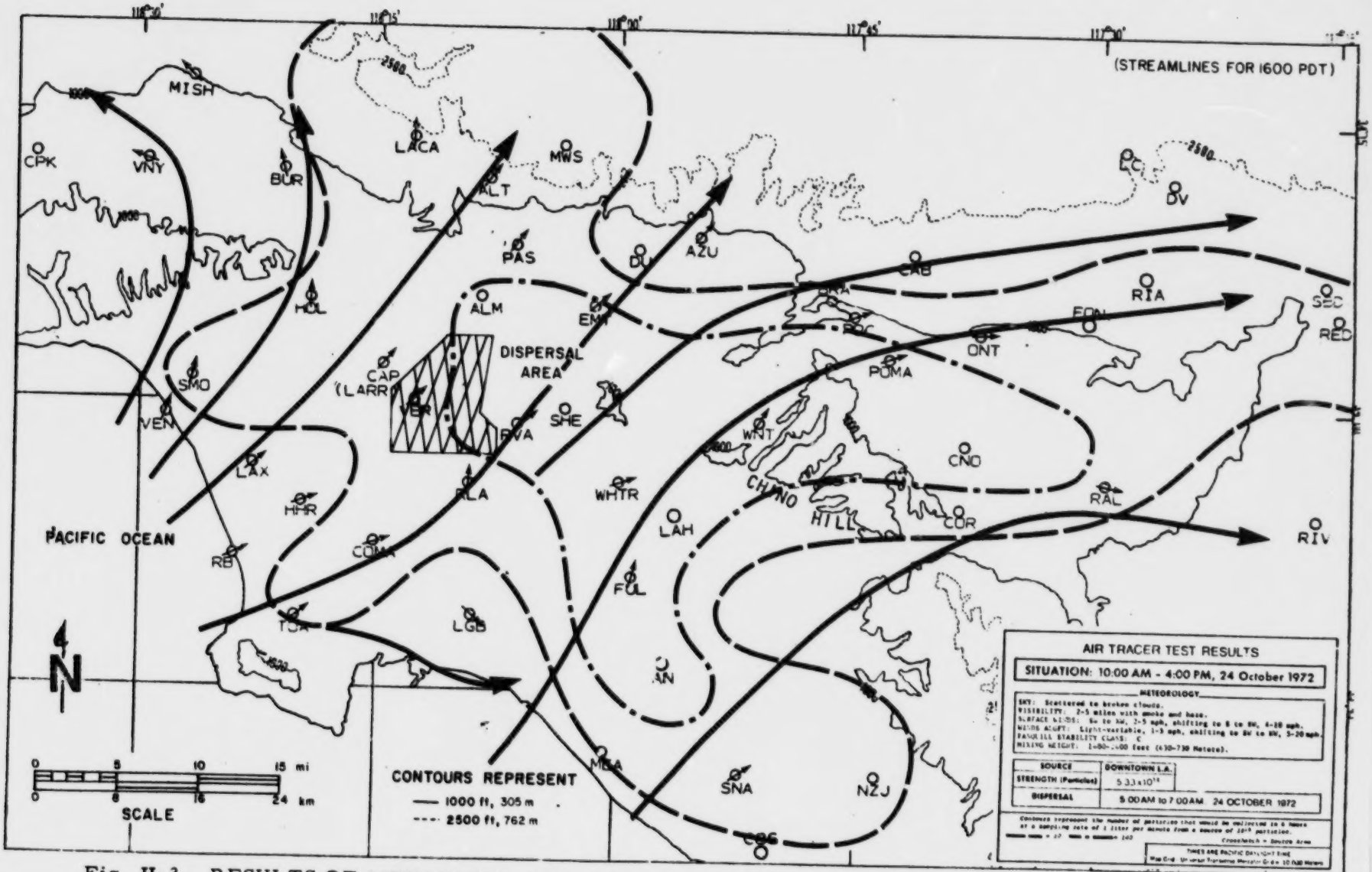


Fig. II-3. RESULTS OF METRONICS, INC. TRACER RELEASE OCTOBER 24, 1972 (Metronics, Inc., 1973) (Contours show average concentration, 1000-1600 PDT, of tracer released in metropolitan Los Angeles area, 0500-0700 PDT.)

On numerous summer and early fall days in 1972 and 1973, instrumented MRI aircraft mapped the three-dimensional distribution of pollutant concentrations in the Los Angeles air basin (Blumenthal et al., 1973, 1974). The sampling consisted of a series of vertical spirals over about 15 different locations in the basin on any given day. Two aircraft were used, and each location was sampled three times per day. Spirals were generally made from the top of the mixing layer or haze layer to the surface. The sampling days were chosen for their high pollution potential, and the aircraft sampling was coordinated with other on-going experiments (such as the Metronics tracer studies) as often as possible. A data package was developed for each sampling day which consisted of the aircraft data as well as surface meteorological data, upper air wind data, and ground level pollution data obtained from all available sources.

Figure II-4 is an example of the vertical profiles produced from the spirals. Pollutant concentrations are plotted versus altitude over Brackett Airport (BRA on Fig. II-1) at about 1707 PDT on July 25, 1973. The scale at the bottom of the figure indicates all the parameters measured, but some of these parameters are often omitted from the graphs for simplicity or because of instrument malfunction. In Fig. II-4, an obvious temperature inversion is present. Pollutants are trapped in the well-mixed layer below the inversion, while concentrations above the inversion are much lower. In general, high, well correlated b_{scat} and ozone levels along with low condensation nuclei and NO_x levels indicate a photochemically aged air mass. High levels of condensation nuclei and primary pollutants (such as CO and NO_x) along with low ozone levels and a poor correlation between b_{scat} and ozone indicate fresh emissions below the inversion level. Below the inversion level, in Fig. II-4, some fresh emissions are mixed into an aged air mass. The air above the mixing layer, although cleaner, includes some well-aged pollutants with no fresh emissions.

A useful technique for studying the total pollutant budget within an air mass is to integrate the pollutant concentration through the depth of the mixing layer, thus obtaining the total pollutant burden over a point on the ground. This technique lets one follow the growth of the pollutant burden in the air mass as the air moves along a trajectory and yet takes into account changes in depth of the mixing layer along the way. The integrals of various pollutants throughout the mixing layer are used in some of the analyses which follow. When aircraft data are available for a given point, an actual integration is performed. In some locations, however, ground data are used to supplement the aircraft data. In these cases, the ground concentration

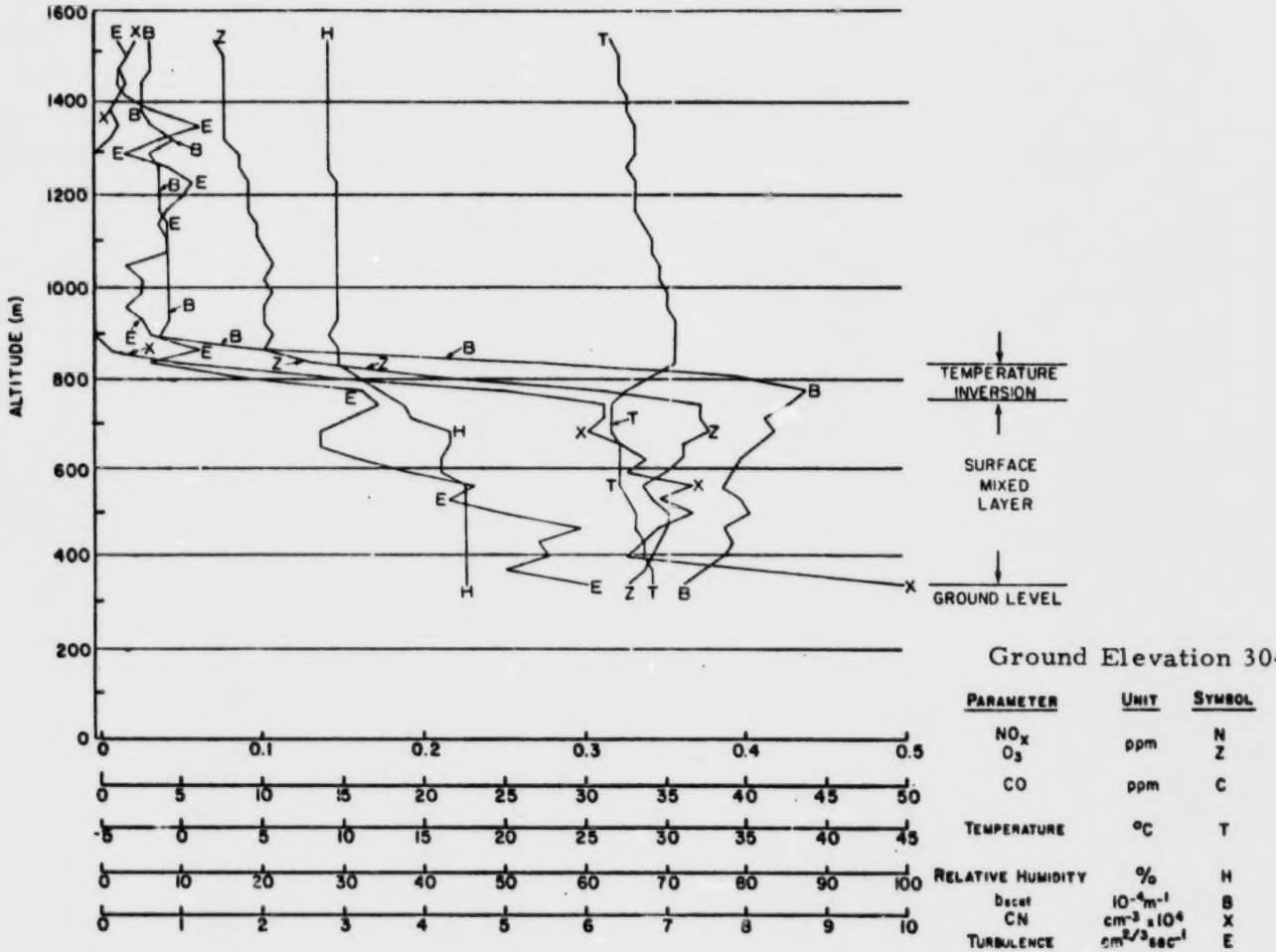


Fig. II-4. VERTICAL PROFILE OVER BRACKETT (BRA) JULY 25, 1973, 1707 PDT

is assumed constant throughout the mixing height and is merely multiplied by the prevailing mixing height in the area. The integral used is given below.

$$L_X = \int_{GL}^{MH} \left([X]_Z - [X]_{BG} \right) \, dZ \qquad (1)$$

In Eq. (1)

X = Any pollutant

$[X]_Z$ = Concentration of X at height Z

$[X]_{BG}$ = Background concentration of X

GL = Ground level

MH = Mixing heights

The integral L_X will be referred to as the loading of X, distinguished from the concentration of X. One effect of correcting for background concentrations in the integral is to render unnecessary the exact determination of mixing height if there is a relatively clean layer above the mixed layer. Background concentrations of 1 ppm for CO and 0.04 ppm for ozone were used in the analyses.

Mixing layer heights were determined from the aircraft soundings. The soundings were examined for points where values of the various meteorological and pollutant parameters decreased (or increased) significantly. In general, turbulence was the primary parameter used, with the b_{scat} profile providing the next best source of information. Temperature and humidity profiles and the vertical profiles of other pollutants were also used. In identifying a top to the mixed layer, as much emphasis as possible was placed on the physical consistency among the various parameters. Discrepancies between the various parametric definitions were reconciled as they appeared. In many situations, the definition of the mixing layer height was simple and unequivocal. In others, the most consistent definition was used.

In the following analyses, surface ozone data obtained from local air pollution districts are used. Since the calibration method used by the L.A. APCD is different from that used by all other agencies in the L.A. Basin, all L.A. APCD ozone data used in this report are adjusted to be consistent with the other agency calibration procedures.

In the remainder of Section A we study the transport of ozone and its precursors from the western basin across the eastern

basin to Redlands, identified by the code RED in Fig. II-1. Our discussion is based on two specimen days for which pollutant loadings in the mixed layer, together with winds aloft and at the surface, were measured.

2. July 25, 1973

a. Summary of Day

July 25, 1973 was the second day of a major smog episode. The California Air Resources Board station at Upland (CAB on Fig. II-5) reported an average ozone concentration of 60 pphm for the hour beginning 1600 PDT, the highest such concentration recorded in the Los Angeles Basin that year. Figure II-5 shows that surface concentrations were generally high in the northern part of the eastern basin at this time.

Meteorological conditions on July 25, 1973 were typical of those associated with heavy smog in the Los Angeles Basin. Throughout the day a strong subsidence inversion covered the whole basin at about 1000 m msl while a marine inversion sloped upward from about 300 m msl near the coast until it merged with the subsidence inversion roughly 40 km inland. The structure of this double inversion is revealed in Figs. II-6 and II-7, which show approximately west to east vertical cross-sections of the light-scattering coefficient, b_{scat}, at the beginning and end of the afternoon. These figures were prepared using the aircraft sounding data at the locations indicated.

During the night and morning hours the surface flow in the basin was either stagnant or had a slight offshore component, allowing the buildup of pollutants within the surface layer. In Fig. II-6, the highest concentrations are seen within the source region in the western basin. Although some of the b_{scat} in this figure is due to humidity effects, much of it results from emissions accumulated in a relatively stagnant air mass. At the time represented in Fig. II-6, the sea breeze had just recently started, and clean air had not yet come onshore to flush out the basin.

Later in the afternoon, as shown in Fig. II-7, the sea breeze had ventilated much of the surface layer in the western basin, replacing air which had had a long residence time over land with cleaner air with a short time onshore. The sea breeze "front" in Fig. II-7 is between El Monte (EMT) and Brackett (BRA). The air just ahead of the "front" had accumulated emissions over the western basin earlier in the day and possibly during the night before, and had the longest residence time over strong source areas of any air in the

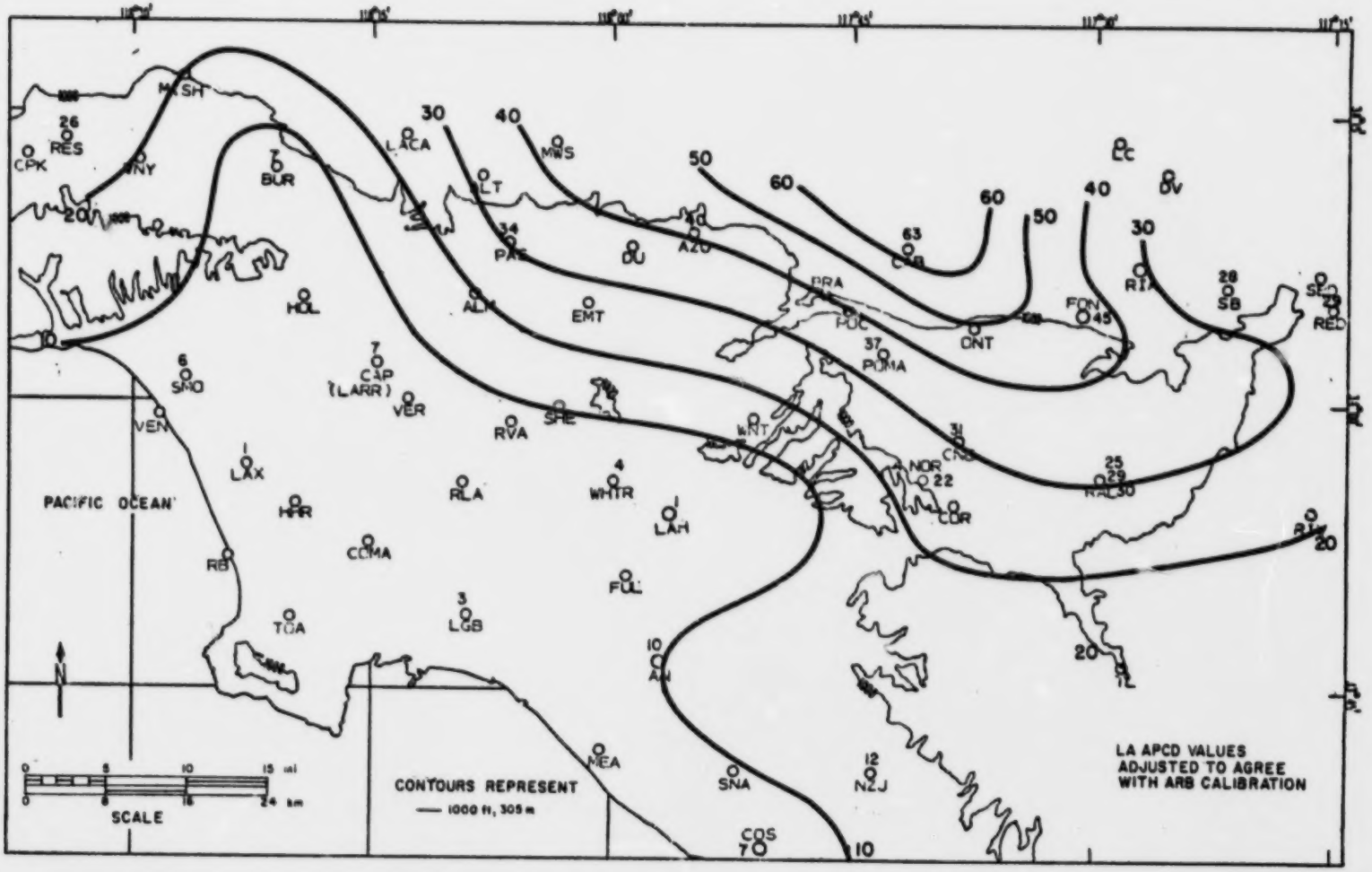


Fig. II-5. SURFACE OZONE CONCENTRATIONS (pphm), 1600-1700 PDT, JULY 25, 1973

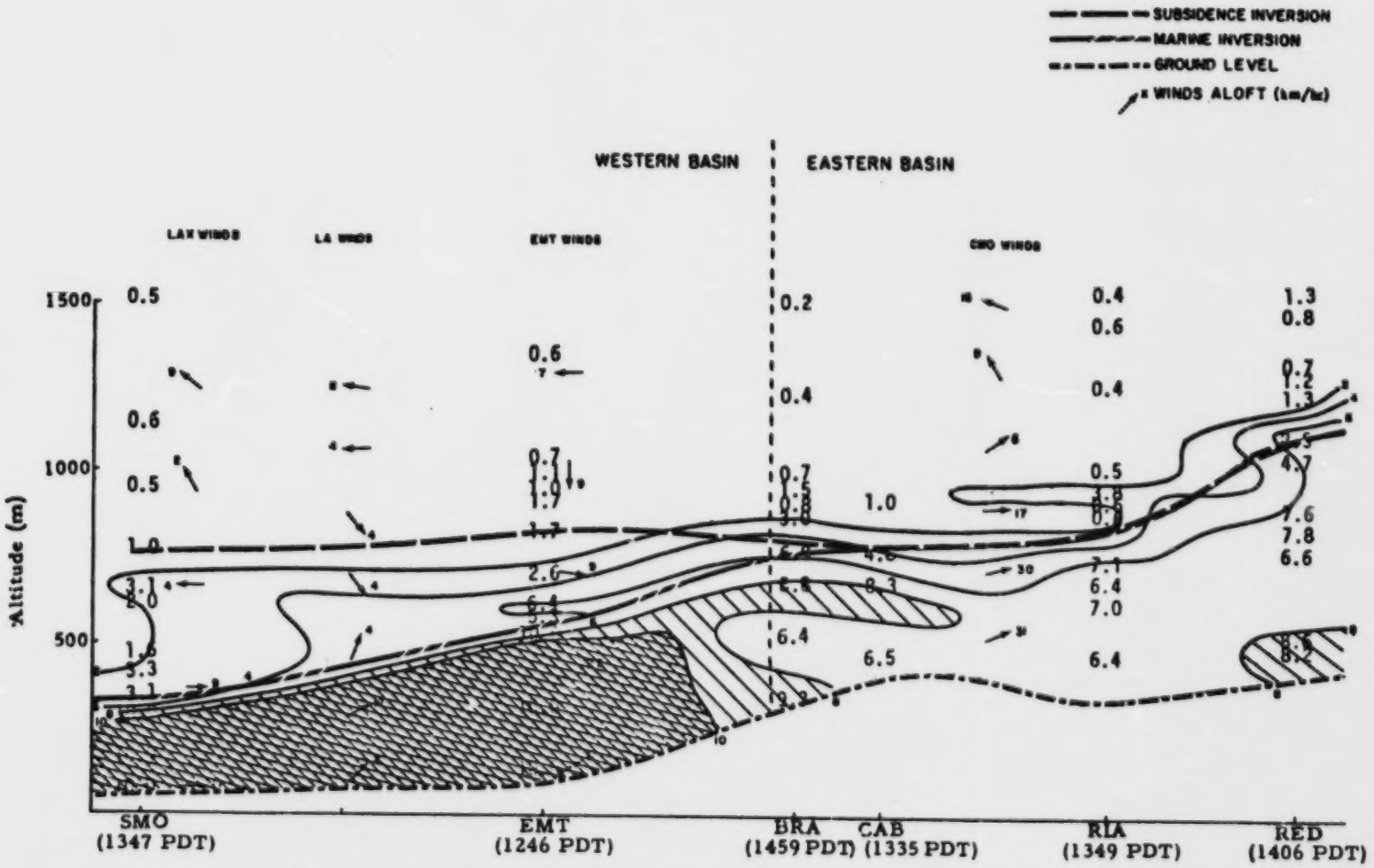


Fig. II-6. VERTICAL CROSS-SECTION OF b_{scat} FOR MIDDAY, JULY 25, 1973
(Units are 10^{-4} m^{-1})

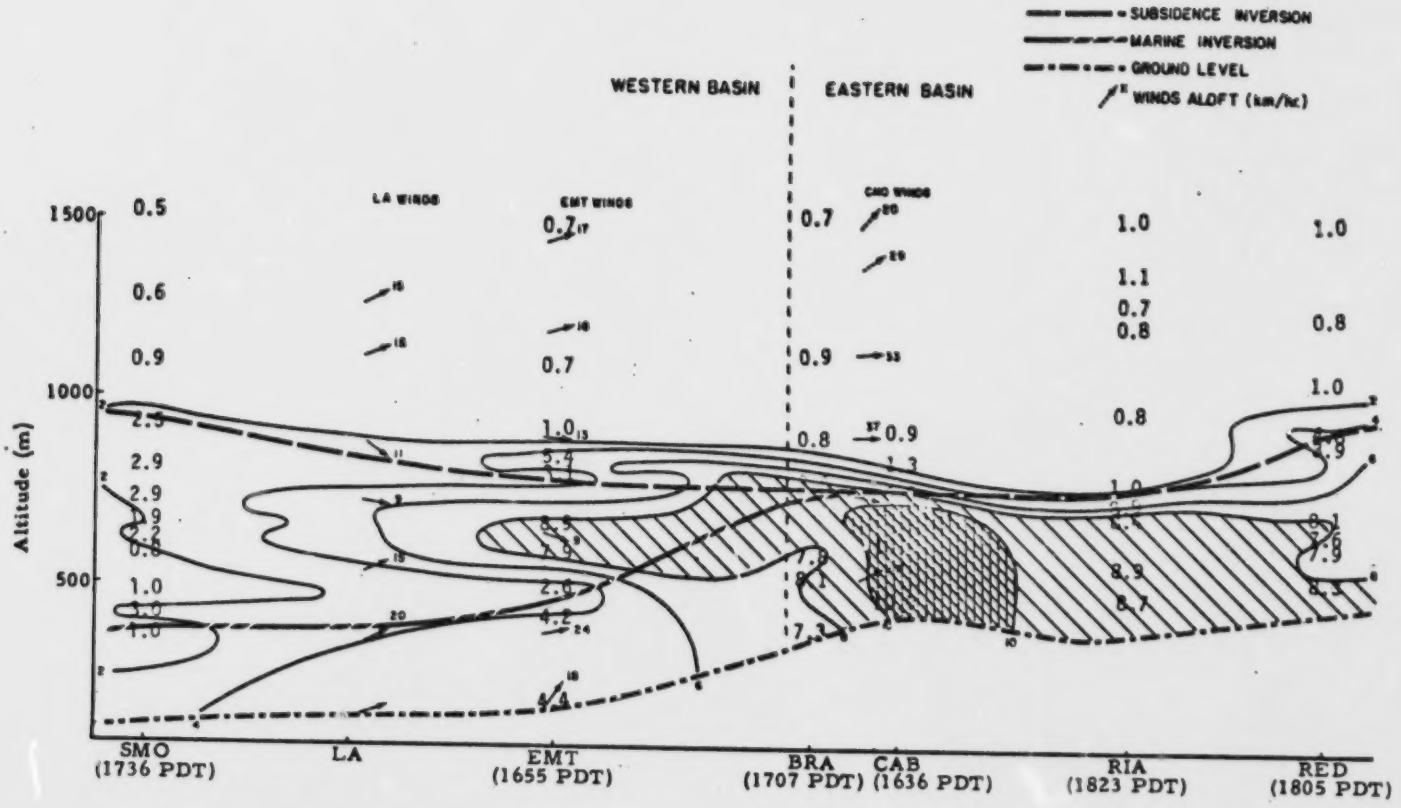


Fig. II-7. VERTICAL CROSS-SECTION OF b_{scat} FOR AFTERNOON OF JULY 25, 1973 (Units are 10^{-4} m^{-1}.)

basin. Note that the highest concentrations in Fig. II-7 are over Upland (CAB) at the time which corresponds to the peak ozone reading at Upland (and in the basin) for the day.

In both Figs. II-6 and II-7 upper layers are seen between the two inversions in the western basin. Pollutant concentrations remain high in the layers all day, but the aircraft sounding and pibal data indicate that these layers are decoupled from the air below. The air in the upper layers is well aged and relatively stagnant compared to surface air. These layers may be caused by upslope flow along some of the nearby hills, by lifting or undercutting of polluted air by the sea breeze, or by other means; but in any case they should not have a significant effect on the results of the analyses presented in this section.

The difference between the air in front of and behind the sea breeze front is seen in Figs. II-8 and II-9. Figure II-8 is a vertical profile over El Monte after the passage of the front. A surface mixing layer is well defined by the temperature, turbulence, and pollutant profiles extending up to about 400 m msl. Within this layer, the b_{scat} and ozone values have dropped down from their peaks for the day. The condensation nuclei values are still high, however, indicating continuing fresh emissions. The air between about 400 and 600 m msl is moderately well aged but still has a moderate condensation nuclei population, possibly indicating that this air was previously part of the surface mixing layer but recently undercut by the advancing sea breeze. The remainder of the layer aloft could be a remnant of the layer existing earlier in the midday soundings.

Figure II-9 is a vertical profile at Upland (CAB) before the passage of the front. The mixing layer is well defined and pollutant concentrations are high within the layer. The ozone concentration exceeds 0.5 ppm. The air within the mixing layer at Upland is similar to that just above the sea breeze in Fig. II-8. This profile represents the period of peak ozone concentration at Upland and in the basin for the day.

b. Trajectory Analysis

Winds aloft on July 25, 1973 were measured at four stationary sites. Pilot balloons (pibals) were released hourly at Chino (CNO), in the eastern basin, and at Elysian Park, midway between Hollywood (HOL) and the Los Angeles Railroad Yard (LARR) in the western basin. In addition, pilot balloons were released at 1233 PDT from Los Angeles International Airport (LAX), and at 1335 and 1654 PDT from El Monte Airport (EMT).

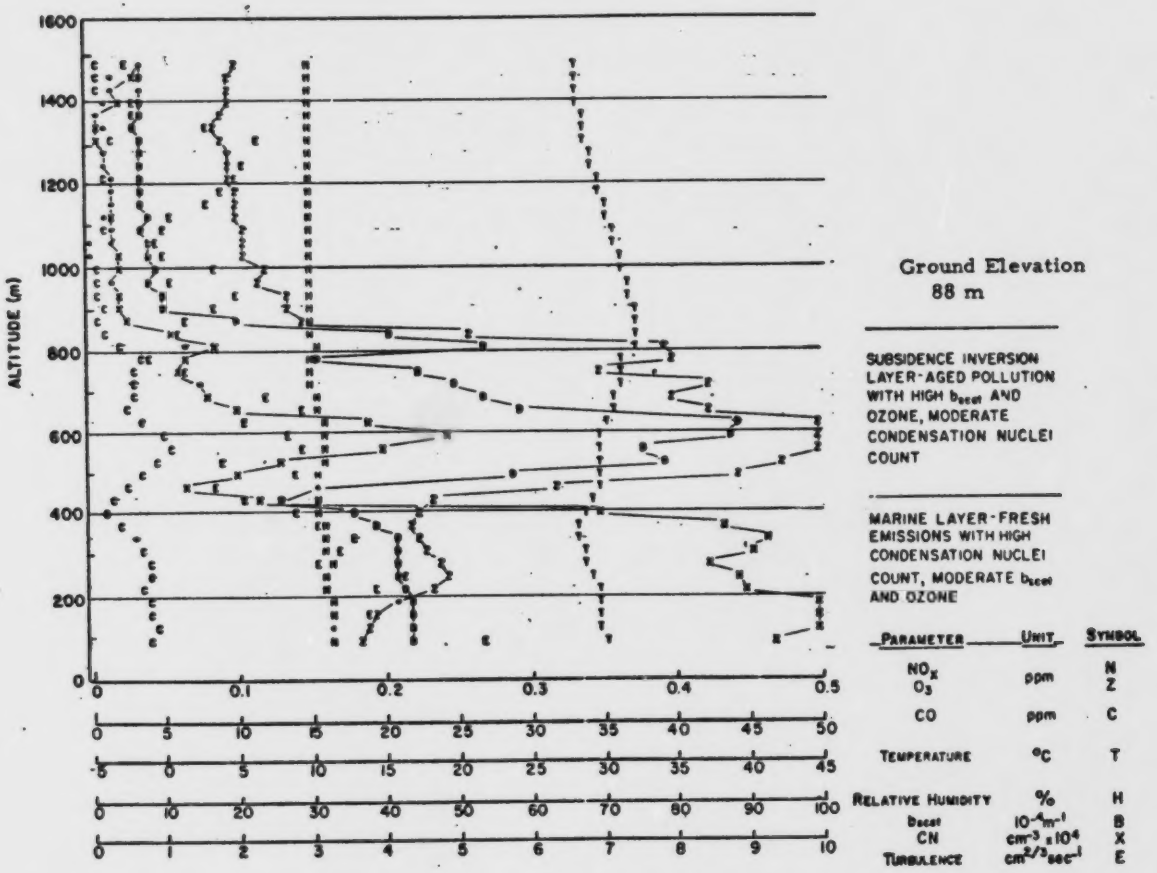

ALTITUDE (m)
1600
1400
1200
1000
800
600
400
200
0
0 0.1 0.2 0.3 0.4 0.5
0 5 10 15 20 25 30 35 40 45 50
-5 0 5 10 15 20 25 30 35 40 45
0 10 20 30 40 50 60 70 80 90 100
0 1 2 3 4 5 6 7 8 9 10
Ground Elevation
88 m
SUBSIDENCE INVERSION LAYER-AGED POLLUTION WITH HIGH b_{scat} AND OZONE, MODERATE CONDENSATION NUCLEI COUNT
MARINE LAYER-FRESH EMISSIONS WITH HIGH CONDENSATION NUCLEI COUNT, MODERATE b_{scat} AND OZONE
PARAMETER UNIT SYMBOL
NO_x ppm N
O_3 Z
CO ppm C
TEMPERATURE °C T
RELATIVE HUMIDITY % H
b_{scat} $10^{-4}m^{-1}$ B
CN $cm^{-3} \times 10^4$ X
TURBULENCE $cm^{2/3}sec^{-1}$ E

Fig. II-8. VERTICAL PROFILE OVER EL MONTE (EMT) JULY 25, 1973, 1655 PDT, AFTER PASSAGE OF SEA BREEZE FRONT

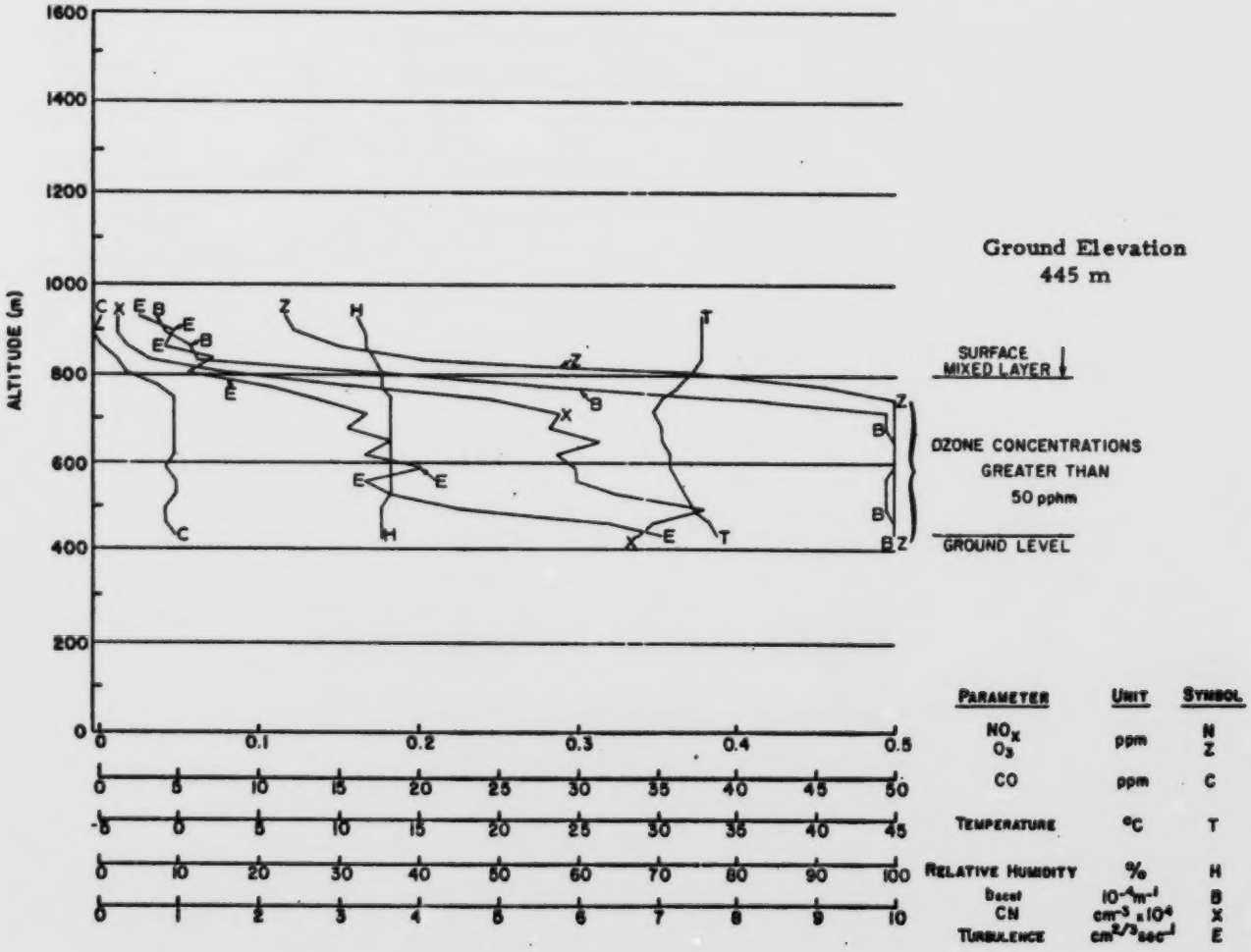


Fig. II-9. VERTICAL PROFILE OVER CABLE (CAB)
JULY 25, 1973, 1636 PDT

Figures II-10 and II-11 show trajectories, computed from these wind observations, for the air arriving over Upland (CAB) at 1600 PDT and Redlands (RED) at 1800 PDT. The extreme northerly and southerly winds within the mixed layer (from pibal observations) were used to construct an envelope of possible trajectories, and the mean wind within the mixed layer was used to construct a characteristic trajectory. Surface wind streamlines for 1600 PDT are shown in Fig. II-12 for reference purposes. The trajectories in Figs. II-10 and II-11 indicate that much of the air over Upland at the time of peak ozone at that location was onshore before the sea breeze started, probably having accumulated pollutants since the night before, while much of the air over Redlands at the end of the afternoon had come onshore with the start of the sea breeze. The air arriving over Upland at 1600 PDT had the longest residence time in the western basin of any air arriving over Upland that day, which may account for the timing of the ozone maximum there.

The streamlines and trajectories indicate that polluted western basin air was advected into the eastern basin during the afternoon of July 25. This conclusion is corroborated by the afternoon gradients in surface ozone concentration, which clearly show the advance of cleaner air from the coast with the onset of the sea breeze. The hourly average surface ozone concentrations from 1600 to 1700 PDT (shown previously in Fig. II-5) provide a snapshot of this effect, showing a strong gradient between La Habra (LAH) and downtown Los Angeles (CAP), which had already been flushed with marine air, and Azusa (AZU) and Upland (CAB), which had not. By 1600 PDT the marine layer had reached El Monte (EMT), and was sharply delineated in a vertical sounding made at 1655 PDT (Fig. II-8).

Figure II-13 shows the approximate times at which the sea breeze began to flush various locations in the basin during the afternoon. These times were determined from California Air Resources Board and local Air Pollution Control Districts (APCD) ozone data according to an objective criterion: the approximate time of arrival of the sea breeze is calculated as M:00 PDT, where M is the first integer i such that $X_{i+1} \leq 1/2\ X_{i-1}$, X_i being the average ozone concentration during the hour beginning at i:00 PDT. Comparison of Fig. II-13 with the trajectories to Upland and Redlands in Figs. II-10 and II-11 shows that these trajectories depict air moving just ahead of the advancing cleaner sea air. From 1600 to 1900 PDT the marine front moved about 70 km inland for an average speed of about 23 km per hour, in good agreement with observed wind speeds.

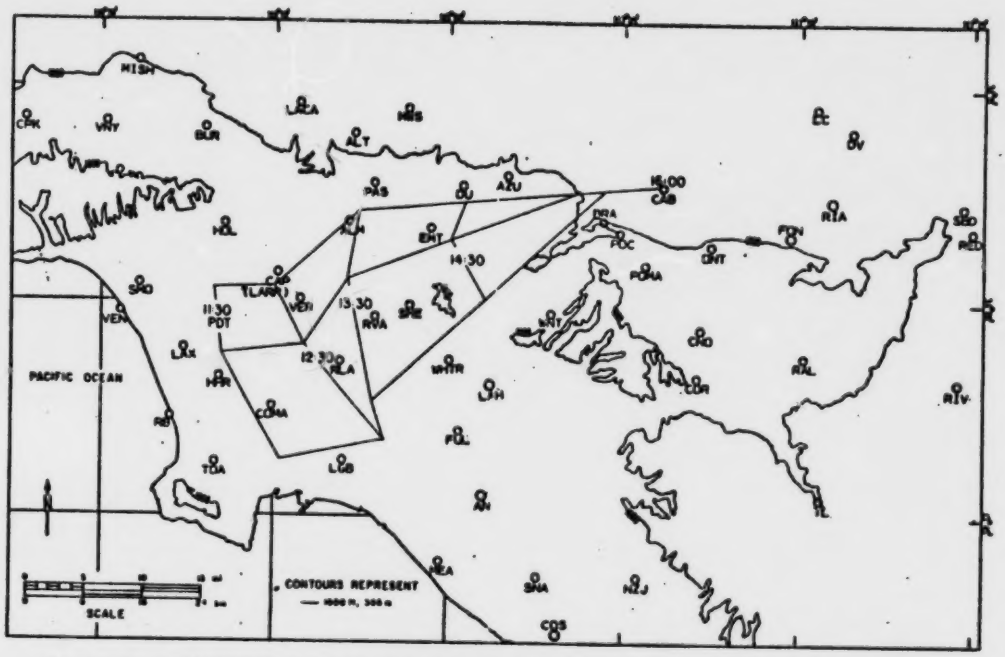


Fig. II-10. TRAJECTORY ENVELOPE FOR AIR ARRIVING AT CABLE AIRPORT (UPLAND) 1600 PDT, JULY 25, 1973

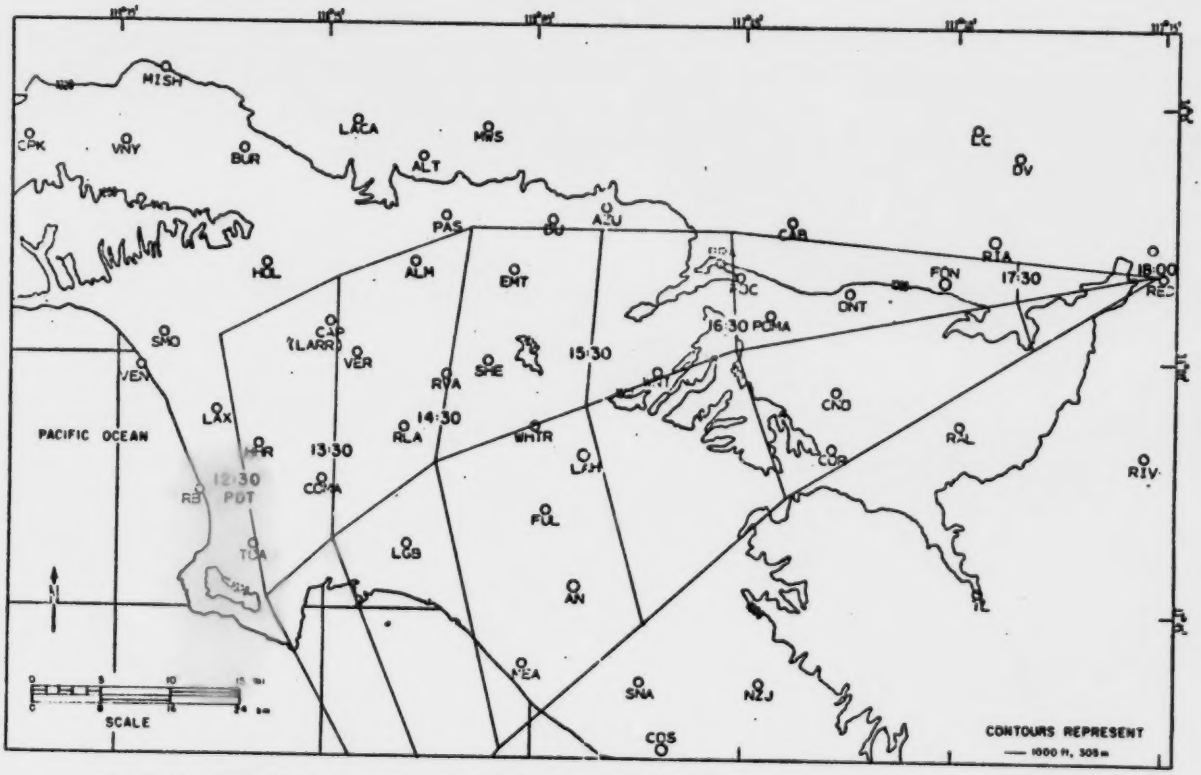


Fig. II-11. TRAJECTORY ENVELOPE FOR AIR ARRIVING OVER REDLANDS AT 1800 PDT, JULY 25, 1973

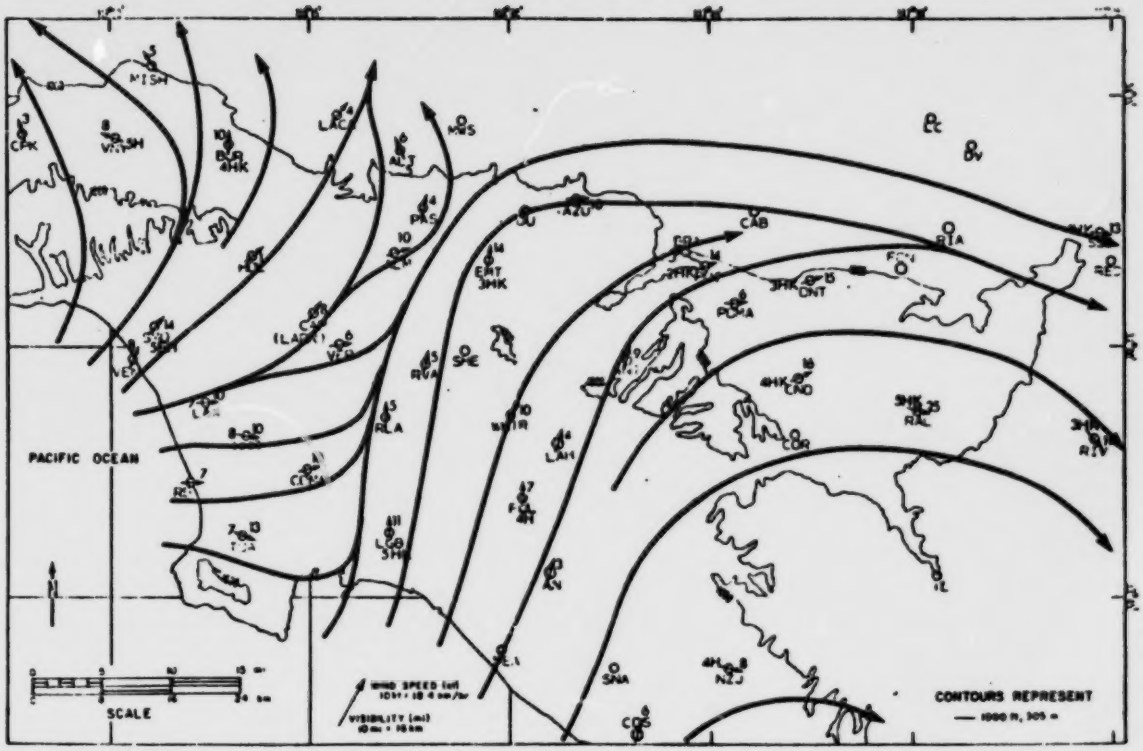


Fig. II-12. SURFACE WIND STREAMLINES - 1600 PDT, JULY 25, 1973

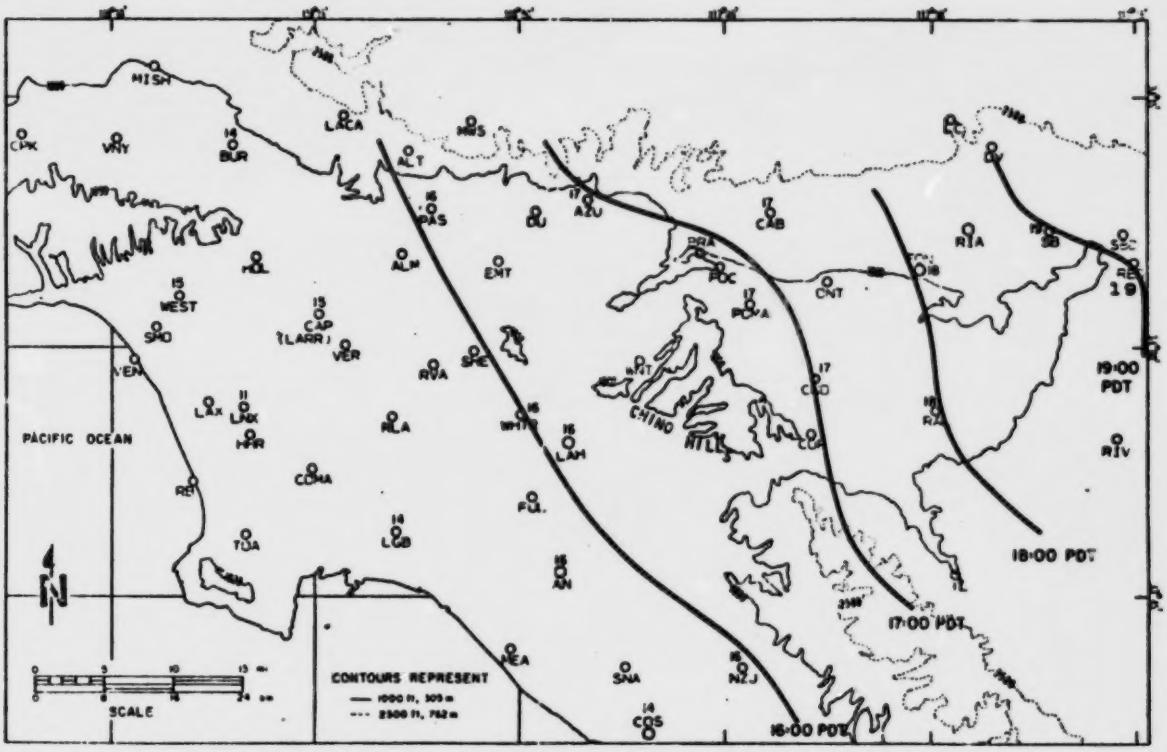


Fig. II-13. APPROXIMATE TIME (PDT) OF ARRIVAL OF SEA BREEZE, JULY 25, 1973
(Objective criterion based on ground level ozone concentrations.)

c. Analysis of Pollutant Data

Figure II-14 shows how integrated contaminant loadings within the surface mixed layer changed along the trajectory to Redlands (RED). Points on the figure were calculated as described earlier in Section II. A. 1, and both surface and aircraft data were used. The aircraft data show that pollutants were well mixed within the mixing layer and that the top of the surface mixing layer was always well defined. The western basin points do not include any contribution from the elevated layers. Data points were calculated for locations in or near the trajectory envelope shown in Fig. II-11.

Although there is considerable scatter in the data, the trends are quite clear. There are large increases in the loadings of CO, O_3, and visibility-reducing particulates between the coast and the boundary between the western and eastern basin (near Brackett (BRA)) across an area which includes most of the emission sources in the Los Angeles Basin. East of Brackett (BRA) loadings of CO actually declined, as local emissions in the eastern basin were apparently not sufficient to offset the effects of dilution or reaction. The emissions in the western basin were sufficient to account for the CO seen along the trajectory in the eastern basin. Ozone loadings east of Brackett remained relatively constant, possibly due to continued formation of ozone by previously emitted precursors and to the lack of fresh emissions to scavenge it.

Nearly all of the CO in the Los Angeles atmosphere comes from the exhaust of motor vehicles (California Air Resources Board 1972). Motor vehicles are also the source of about 75 percent of the NO_x and 87 percent of the reactive hydrocarbons (Calif. ARB, 1972). Using CO as a tracer for ozone precursors which were not measured directly, we can deduce that a large fraction of the ozone precursors introduced into the air mass sampled at Redlands was emitted in the western basin.

Additional information on the amount of ozone transported into the eastern basin can be obtained by doing a simple flux calculation. Figure II-15 shows an estimate of the flux of ozone under the subsidence inversion from the western basin into the eastern basin at 1700 PDT on July 25. The western face of the box drawn in the eastern basin represents the boundary across which transport was calculated, and the east-west dimension of the box represents the distance covered in one hour by the moving air. In a steady-state situation in the absence of diffusion or diffluent winds, the box would thus contain about 185 metric tons of ozone, corresponding to a uniform concentration of about 25 pphm. For comparison, the average late afternoon concentrations

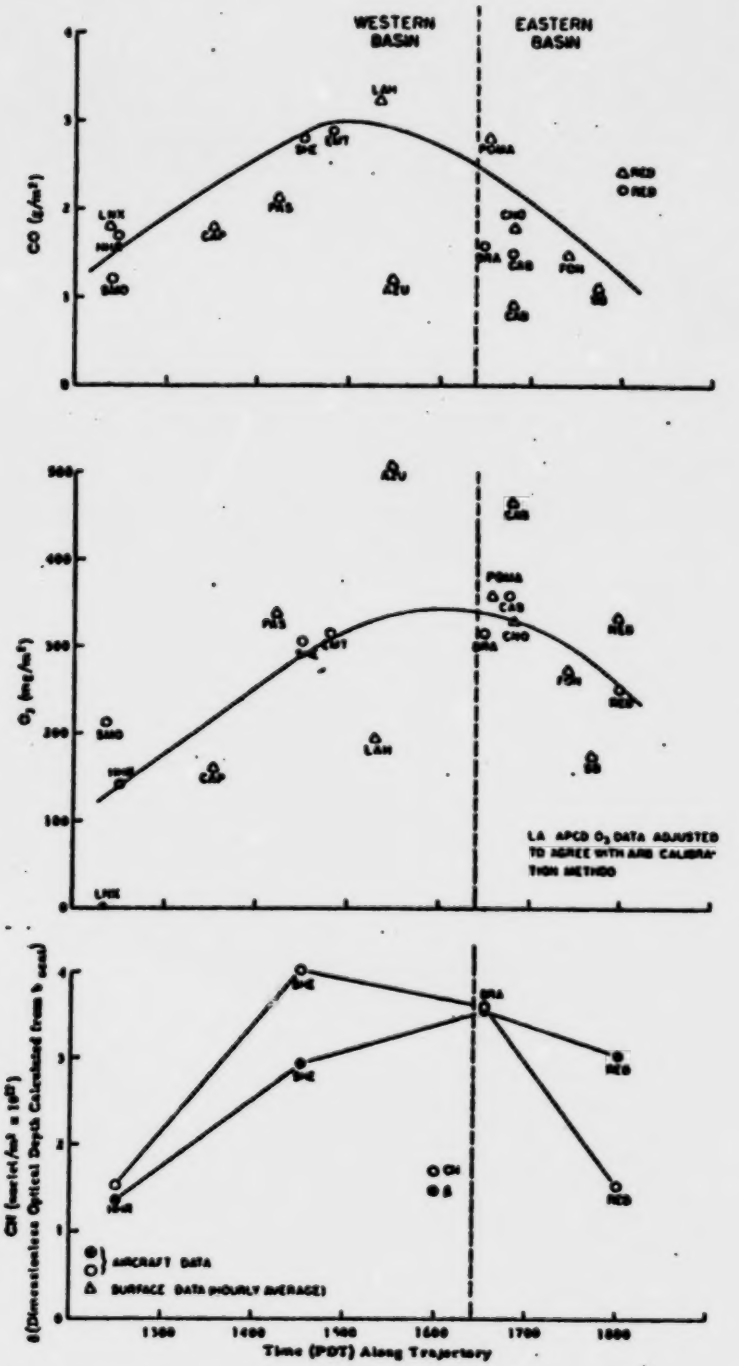


Fig. II-14. POLLUTANT LOADINGS IN SURFACE MIXED LAYER ALONG TRAJECTORY ARRIVING AT REDLANDS IN AFTERNOON OF JULY 25, 1973

(Aircraft measurements plus estimates made from ground data and mixing height.)

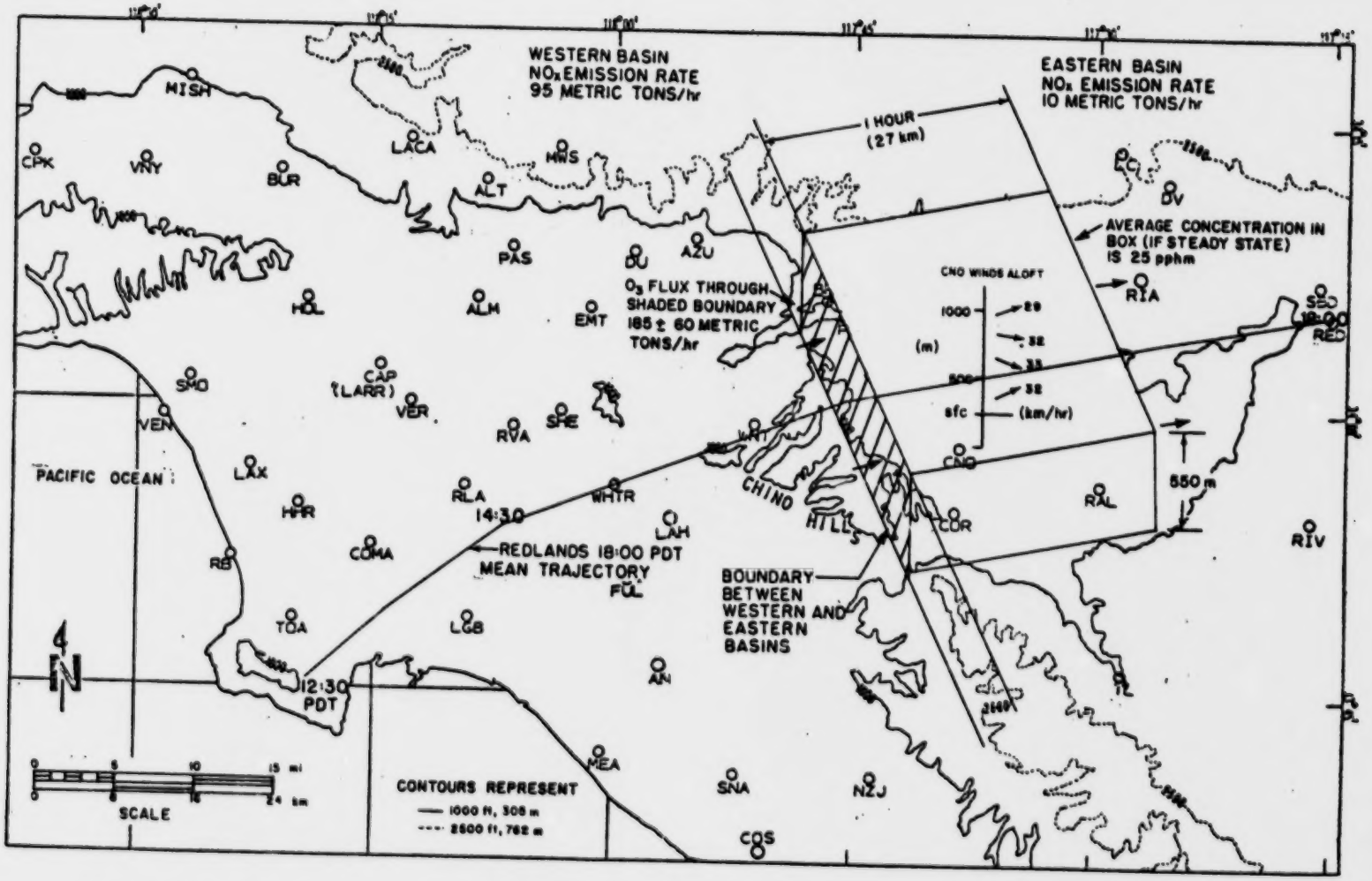


Fig. II-15. ESTIMATED OZONE FLUX FROM WESTERN TO EASTERN BASIN, JULY 25, 1973 1700 PDT

of ozone within the surface mixed layer at Riverside (RAL), Redlands (RED), Rialto (RIA), and Ontario (ONT) were, respectively, 36, 24, 25, and 13 pphm. (Data were taken from aircraft soundings.) The flux was calculated for about 1700 PDT since soundings were available for roughly that time, but 1700 PDT was also roughly the time of arrival of the sea breeze front. Crude flux calculations for about 2 hours earlier indicated slightly greater flux and a correspondingly higher average concentration in the box.

In the absence of photochemistry, one ton (as NO_2) of freshly emitted NO_x (mostly NO) could scavenge about one ton of ozone under conditions of good mixing. The daily emissions of NO_x in the entire eastern basin are estimated to be only about 120 metric tons. Roth et al., (1974) found that in the western basin, about 16 percent of a weekday's total car mileage was driven between 1600 and 1800 PDT. If this 8 percent per hour figure is used to scale all NO_x emissions to hourly rates (for around 1700 PDT) one obtains an estimate of 10 metric ton per hour for the NO_x emission rate in the eastern basin. This is inadequate to scavenge more than a small fraction of the ozone advected in.

The estimate of the ozone flux and the corresponding average concentration in the eastern basin "box" were based on the following considerations:

1. A quasi-steady state prevailed for at least one hour at the boundary between the basins. This assumption was quite good at the boundary even though this was not the case over the whole western basin as the progress of the sea breeze in Fig. II-13 shows. Pollutants which had accumulated in the western basin for many hours were flushed out into the eastern basin by the sea breeze starting about midday. For this reason, pollutant fluxes out of the western basin are not directly comparable to pollutant emissions within the western basin. The western basin was "emptied" more rapidly than it was "filled", giving rise to fluxes which were large in comparison with emission rates.

2. Afternoon soundings at Brackett (BRA) (Fig. II-16) and Corona (COR) (Fig. II-17) showed a capping subsidence inversion at about 860 m msl. Ground elevations east of the Chino Hills slope from roughly 310 m msl at Brackett to 165 m msl at Corona; the Chino Hills themselves range 400-500 m msl, and the width of the pass between the western and eastern basins is 25-35 km. The area across which the flux was calculated was taken as 25 km x (860 m - 310 m) $\simeq 1.4 \times 10^7$ m^2.

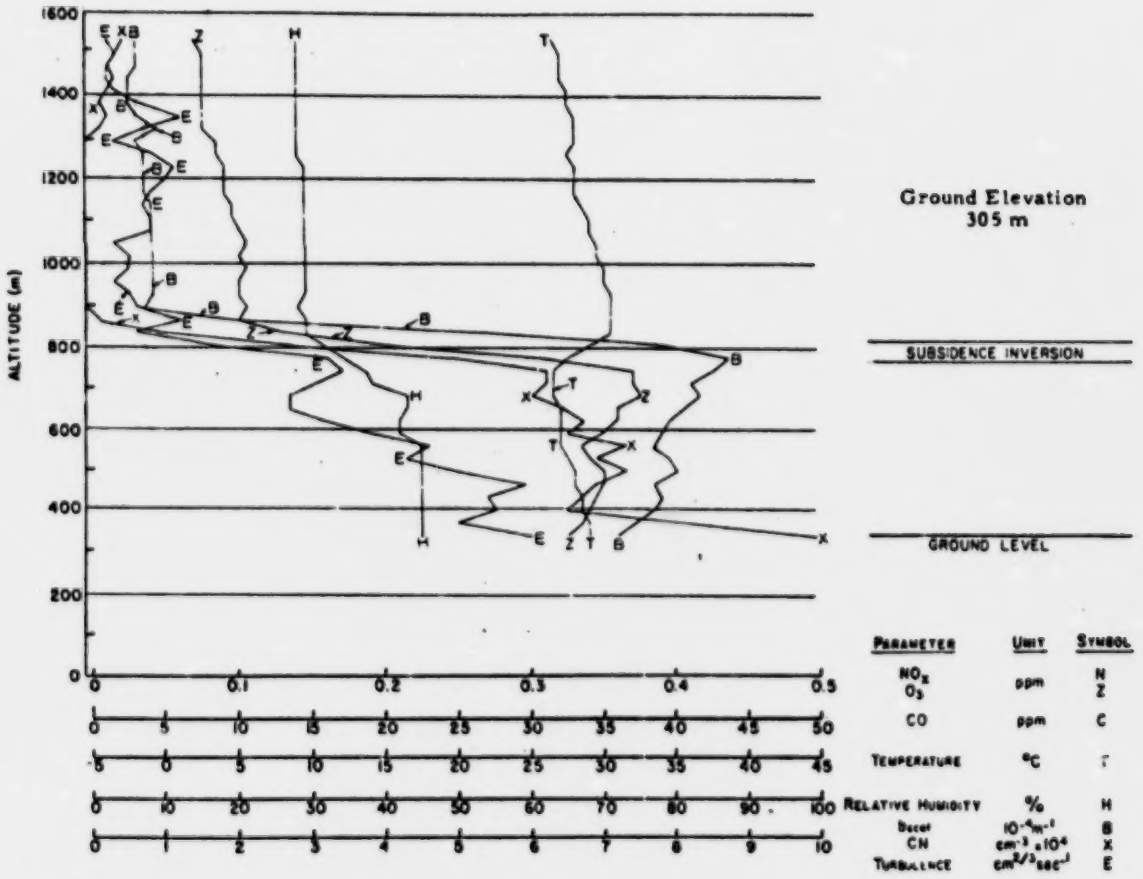


Fig. II-16. VERTICAL SOUNDING AT BRACKETT (BRA) JULY 25, 1973, 1707 PDT

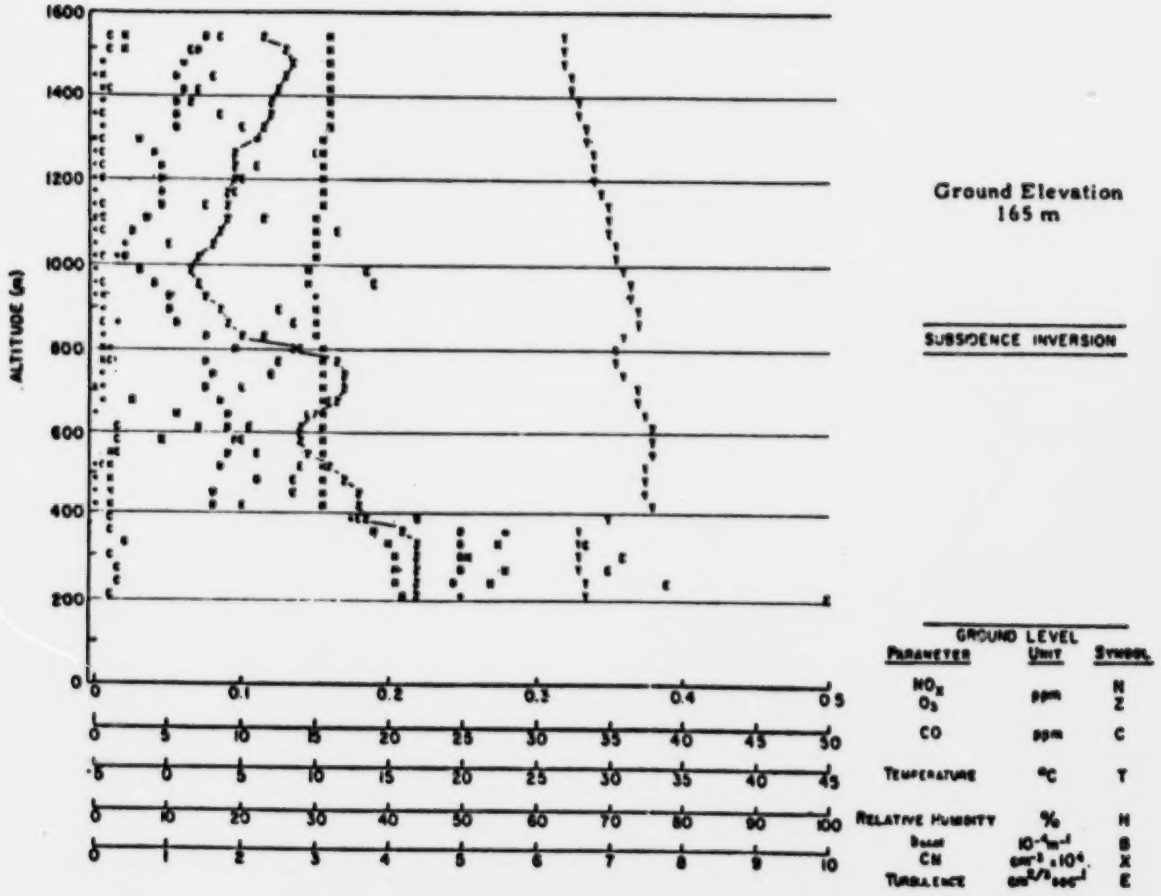


Fig. II-17. VERTICAL PROFILE OVER CORONA (COR) JULY 25, 1973, 1724 PDT

3. The 1700 PDT winds aloft at Chino (CNO) were above 32 km per hour throughout the mixed layer, and the 1700 PDT surface winds at Chino, La Verne College (POC), and Ontario (ONT) were all 27 km per hour. All wind directions in this area were near due west. The rate at which air was transported into the eastern basin was taken to be:
1.4×10^7 m^2 x 27 km/hr $\simeq$ 3.8×10^{11} m^3/hr.
The average ozone concentrations measured between 310 and 860 m msl on the 1700 PDT Brackett and Corona soundings were, respectively, 33.5 pphm = 660 μg/m^3 and 16.8 pphm = 330 μg/m^3. These were slightly lower than the corresponding values for the 1500 PDT soundings. The distribution of ozone concentrations at the surface indicates that concentrations between Brackett and Corona were generally intermediate in value. The rate at which ozone was advected into the eastern basin was estimated to lie between 3.8×10^{11} m^3/hr x 660 μg/hr $\simeq$ 250 metric tons/hr. and
3.8×10^{11} m^3/hr x 330 μg/hr $\simeq$ 125 metric tons/hr.

Using this crude technique, it is clear that much of the ozone loading in the eastern basin on the afternoon of July 25 can be accounted for by advection from the western basin. In light of the preceding analyses, it is probable that a significant portion of the 24 pphm of ozone within the mixed layer arriving at Redlands at about 1800 PDT had its origin in the western basin. Redlands is approximately 100 km from the area south of Los Angeles where the trajectory originated, thus it is reasonably certain that large source areas such as Los Angeles and Orange counties can and do export a significant amount of ozone and ozone precursors to distant surrounding areas.

July 25, 1973, was used in this analysis since a considerable amount of data was available for that day, but similar evidence can be provided for numerous days in the Los Angeles Basin. In Section II. A. 3, following, another day is analyzed in less detail to support the conclusions reached here.

Soundings and other data used in this analysis and not presented here are included in Appendix A.

3. September 21, 1972

a. Summary of Day

September 21, 1972 was a day of relatively light smog. Pollutants were mixed through a deep layer inland, due to intense surface heating. Surface O_3 concentrations were generally below 20 pphm, and the highest concentration encountered aloft was 33 pphm.

Figure II-18 shows the peak ozone concentrations measured within the mixing layer in the midday (1230 - 1430 PDT) aircraft soundings. The morning winds aloft were generally northerly, and the highest ozone concentrations and loadings measured were found in the southern part of the western basin. Figure II-19 shows the changed situation observed in the afternoon (1600 - 1800 PDT) soundings. The eastern basin, which was quite clean at midday due to Santa Ana (northeasterly) winds continuing from September 20, developed elevated ozone concentrations throughout the mixed layer in the afternoon. The portion of the western basin sampled had, meanwhile, cleared out considerably with the advent of the sea breeze which developed after the Santa Ana condition subsided.

b. Trajectory Analysis

Extensive observations of winds aloft were made on September 21, 1972 as part of the Metronics tracer study mentioned earlier, although no tracer was released on this date. From 0700 to 1800 PDT, one pilot balloon was released each hour from each of four locations which moved along routes shown in Fig. II-20 as a series of squares. The release locations were intended to approximately follow air parcel trajectories, beginning in the western part of the basin in the morning and ending in the eastern sections by late afternoon.

Figure II-20 shows trajectories, computed from these wind observations, for the air arriving at Redlands at 1730 PDT. As for July 25, 1973, the extreme northerly and southerly winds within the mixed layer were used to construct an envelope of possible trajectories, and the vector mean wind within the mixed layer was used to construct a characteristic trajectory. As shown in Fig. II-20, a probable track of the air arriving at Redlands is from the industrial section south of Los Angeles through Pomona and Ontario to Redlands. Surface wind streamlines during the afternoon (Fig. II-21) support this conclusion.

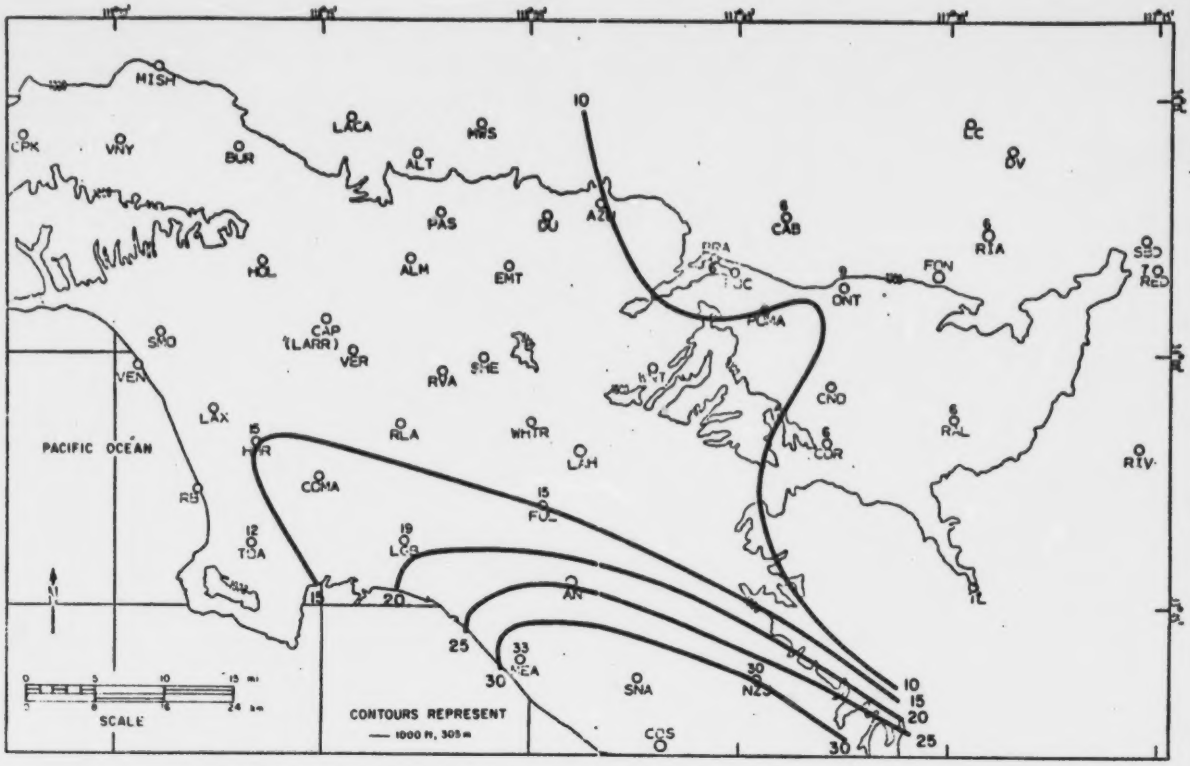


Fig. II-18. PEAK OZONE CONCENTRATIONS (pphm) ALOFT AT MIDDAY, SEPTEMBER 21, 1972, 12:30 - 14:30 PDT

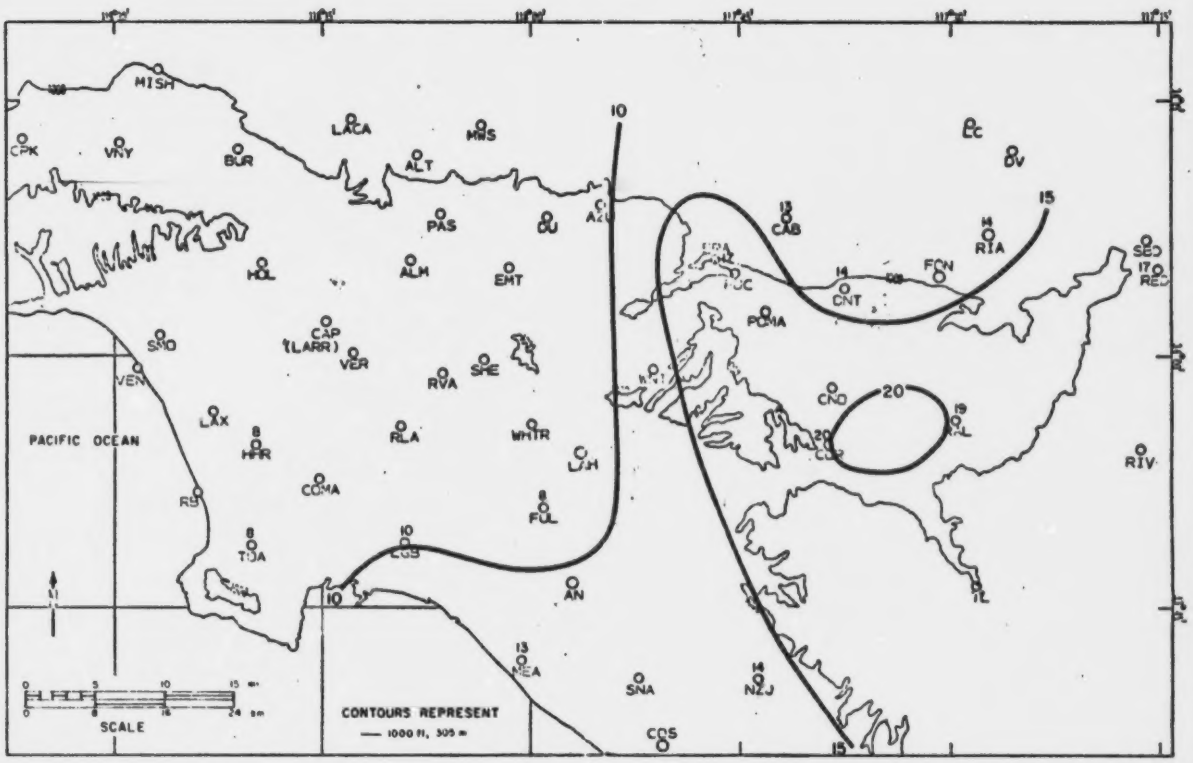


Fig. II-19. PEAK OZONE CONCENTRATIONS (pphm) ALOFT IN LATE AFTERNOON SEPTEMBER 21, 1972

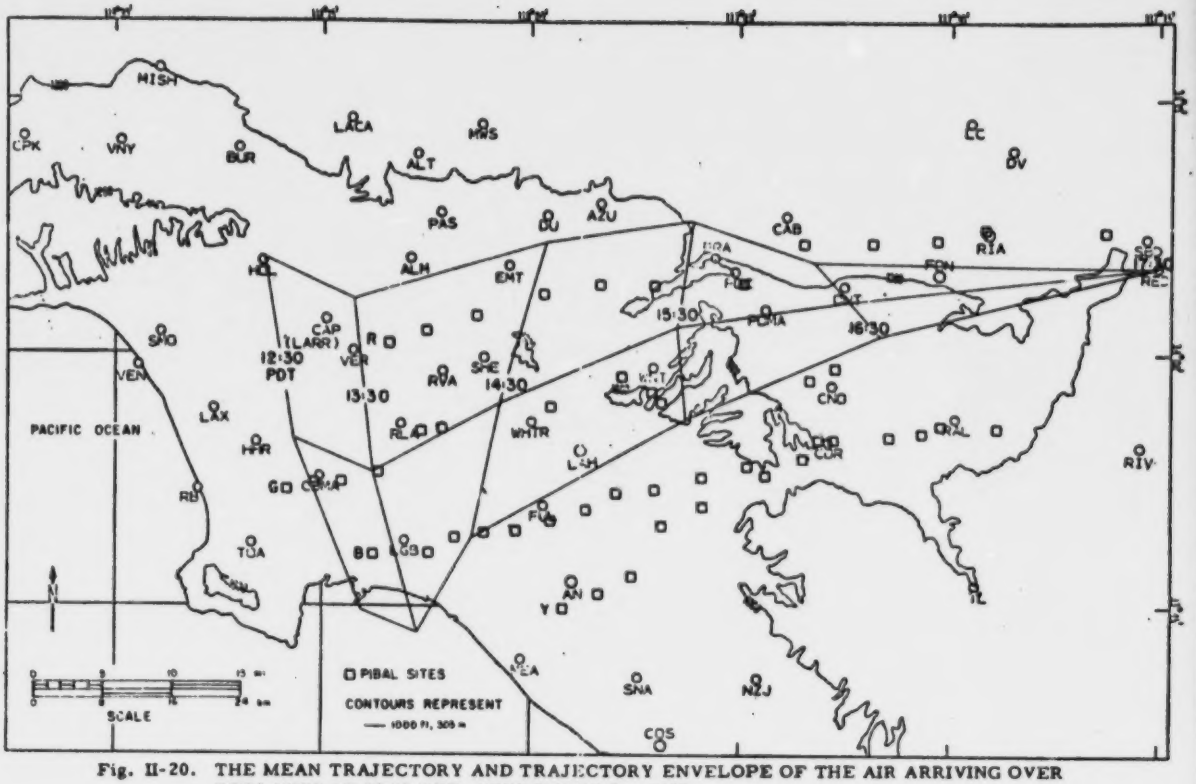


Fig. II-20. THE MEAN TRAJECTORY AND TRAJECTORY ENVELOPE OF THE AIR ARRIVING OVER REDLANDS AT 17:30 PDT, SEPTEMBER 21, 1972
(Times along the trajectory are the times the air passed that line.)

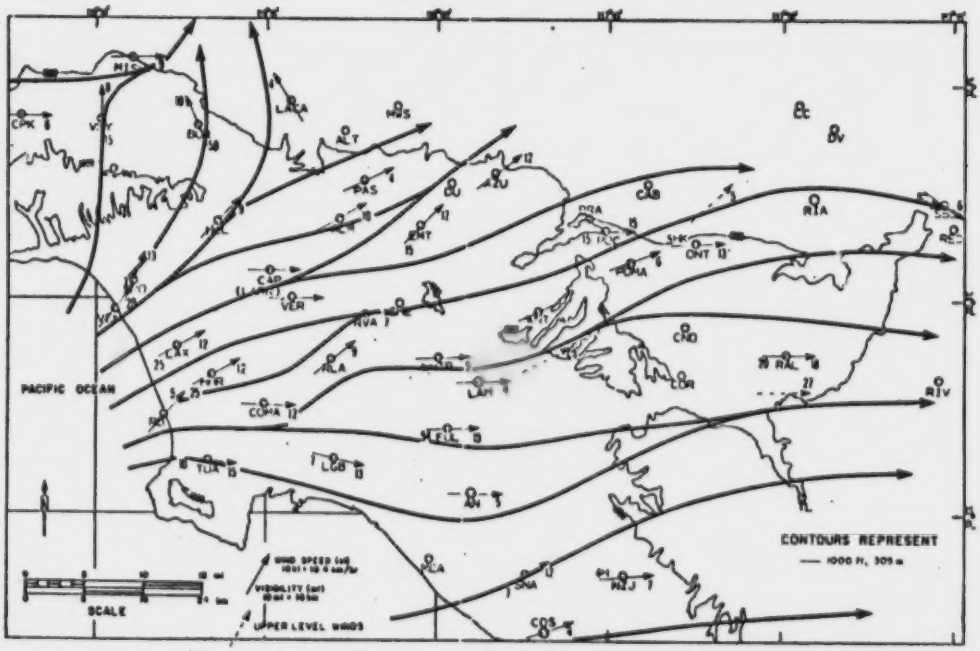


Fig. II-21. STREAMLINE ANALYSIS - 1600 PDT, SEPTEMBER 21, 1972

c. Analysis of Pollutant Data

Figures II-22 and II-23 compare soundings made over Redlands at 1320 and 1736 PDT on September 21, 1972. The light-scattering coefficient observed on the midday flight was below 10^{-4} m^{-1} at all levels, and indicated a local visual range of 55 km (35 miles) or more. By afternoon, the light-scattering coefficient was about 4×10^{-4} m^{-1} at all levels, corresponding to a local visual range of about 10 km (6 miles).

The appearance late in the day of elevated O_3 and b_{scat} concentrations in the eastern basin is difficult to understand in terms of local sources. No inversion was present during the afternoon in the eastern basin to hold reactants near the ground at high concentrations. There was less solar energy to drive reactions in the afternoon than there had been at midday. There is no reason to assume that diurnal patterns of emissions in the eastern basin are dramatically different from those in the western basin, where O_3 concentrations nearly always decrease during the afternoon.

The afternoon increase of O_3 concentrations in the eastern basin is most easily explained in terms of advection, since most of the eastern basin air sampled in the afternoon sounds was passing through the western basin during the midday soundings. Figure II-20 shows that the air in the 1736 sounding at Redlands (RED) was apparently just entering the eastern basin through the pass at La Verne (POC) when the 1625 sounding was taken at nearby Brackett Airport (BRA). During the midday soundings, some of this same air may have been as far west as Long Beach (LGB) and downtown Los Angeles (CAP).

Figures II-23, II-24 and II-25 show aircraft soundings taken at Long Beach (1352 PDT), (Brackett 1625 PDT), and Redlands (1736 PDT), corresponding roughly to the itinerary outlined above. Figure II-26 shows how integrated contaminant loadings (L_x) changed along this route. The aircraft soundings did not reach the top of the polluted layer (shown to be about 2000 m msl in other soundings) at Redlands, and an arbitrary mixing height which encompassed the bulk of the CO was chosen for the computations at this location. Since only three aircraft data points were available, ground level data were also used in preparing Figure II-26. Ground concentrations were assumed constant throughout the prevailing mixing height in the area.

A considerable amount of scatter is evident in the ground data. Much of this results from the complicated flow on this day in the vicinity of passes. In addition, the effects of local sources on the loadings calculated from ground data are accentuated in the eastern basin, due to the great depth of the surface mixed layer there. The general trend of the data, however, is in agreement with the results of the better-defined situation on July 25, 1973.

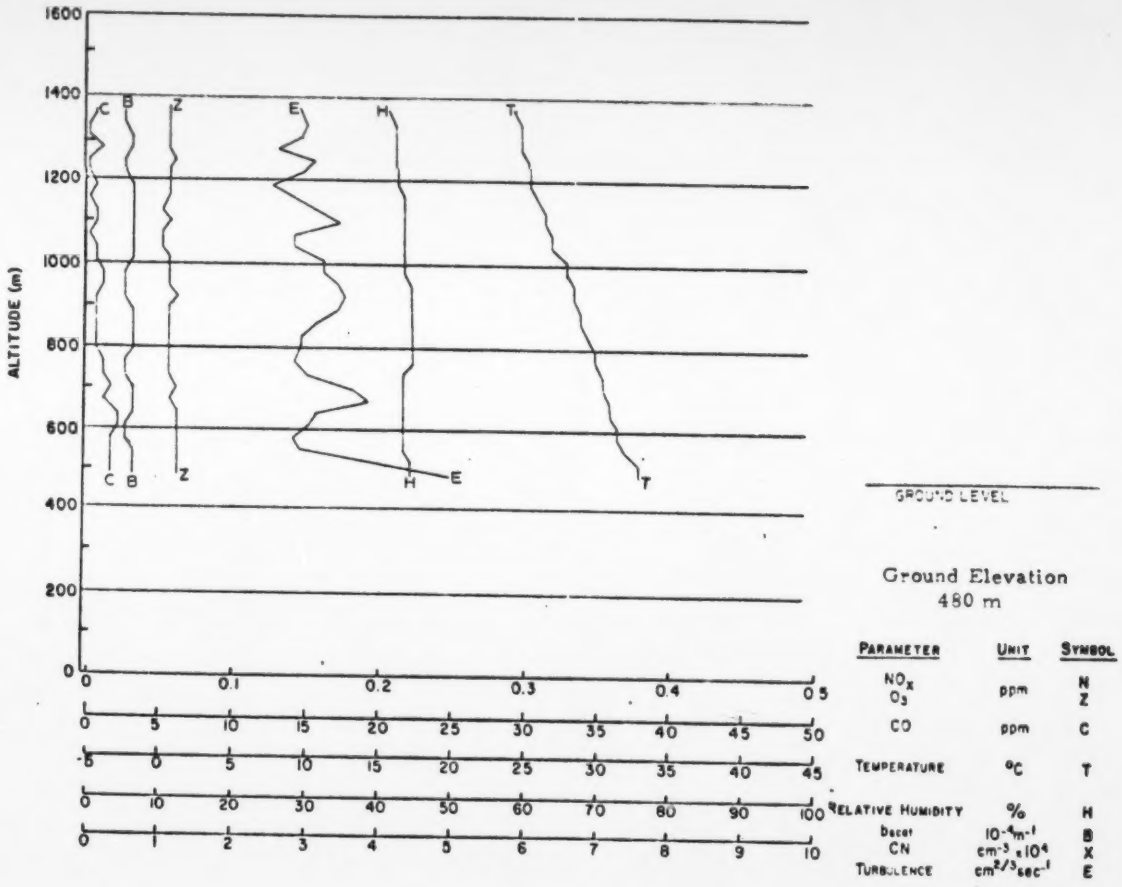


Fig. II-22. VERTICAL PROFILE OVER REDLANDS (RED) SEPTEMBER 21, 1972, 1320 PDT

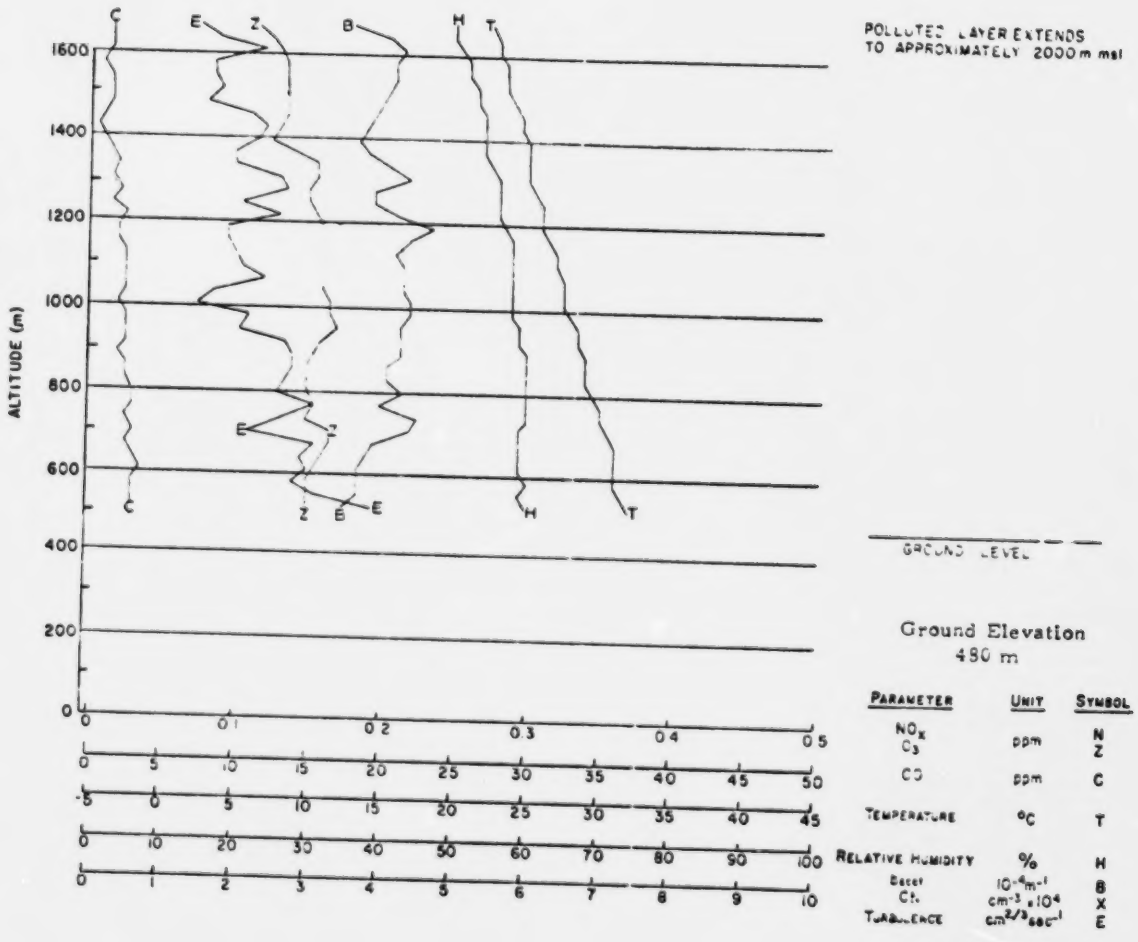


Fig. II-23. VERTICAL PROFILE OVER REDLANDS (RED) SEPTEMBER 21, 1972, 1736 PDT

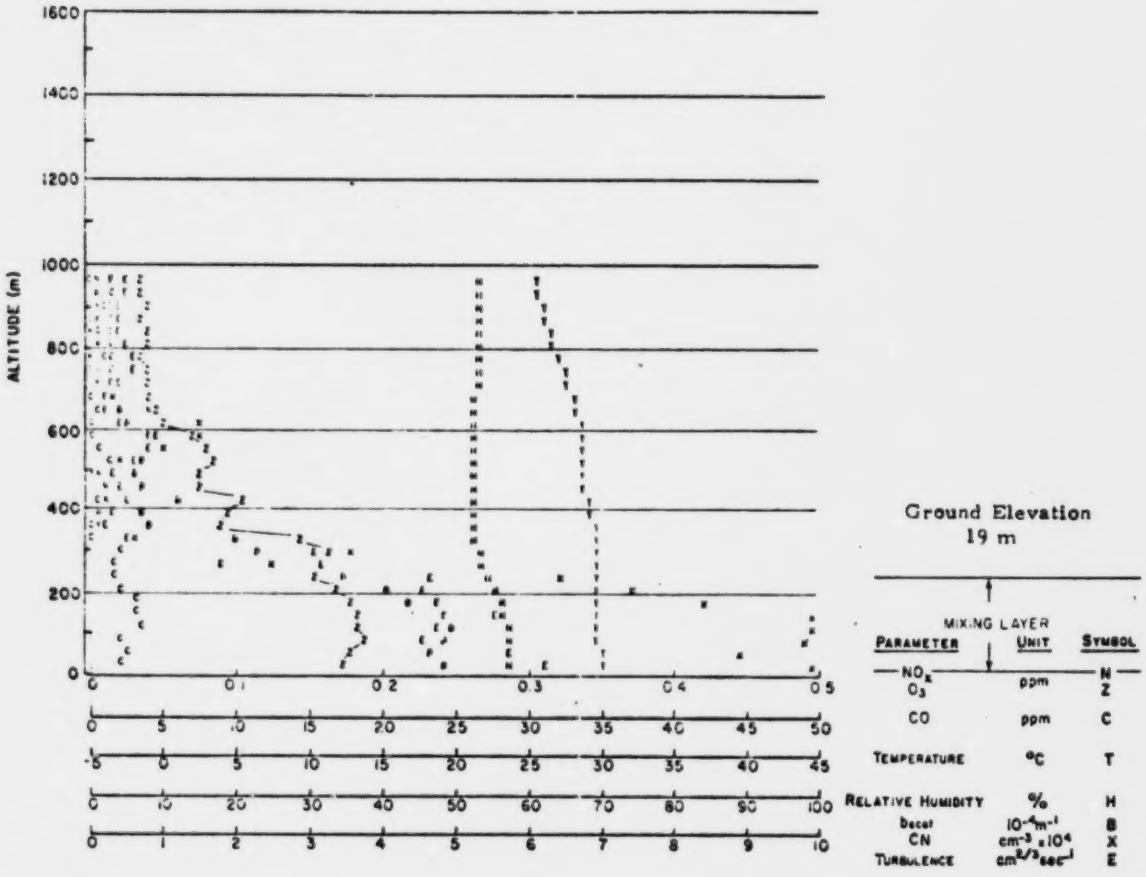

ALTITUDE (m)
1600
1400
1200
1000
800
600
400
200
0
0 0.1 0.2 0.3 0.4 0.5
0 5 10 15 20 25 30 35 40 45 50
-5 0 5 10 15 20 25 30 35 40 45
0 10 20 30 40 50 60 70 80 90 100
0 1 2 3 4 5 6 7 8 9 10
Ground Elevation
19 m
MIXING LAYER
PARAMETER | UNIT | SYMBOL
NO_x | ppm | N
O_3 | ppm | Z
CO | ppm | C
TEMPERATURE | °C | T
RELATIVE HUMIDITY | % | H
bscat | $10^{-4}m^{-1}$ | B
CN | $cm^{-3} \times 10^4$ | X
TURBULENCE | $cm^{2/3}sec^{-1}$ | E

Fig. II-24. VERTICAL SOUNDING OVER LONG BEACH (LGB) SEPTEMBER 21, 1972, 1352 PDT

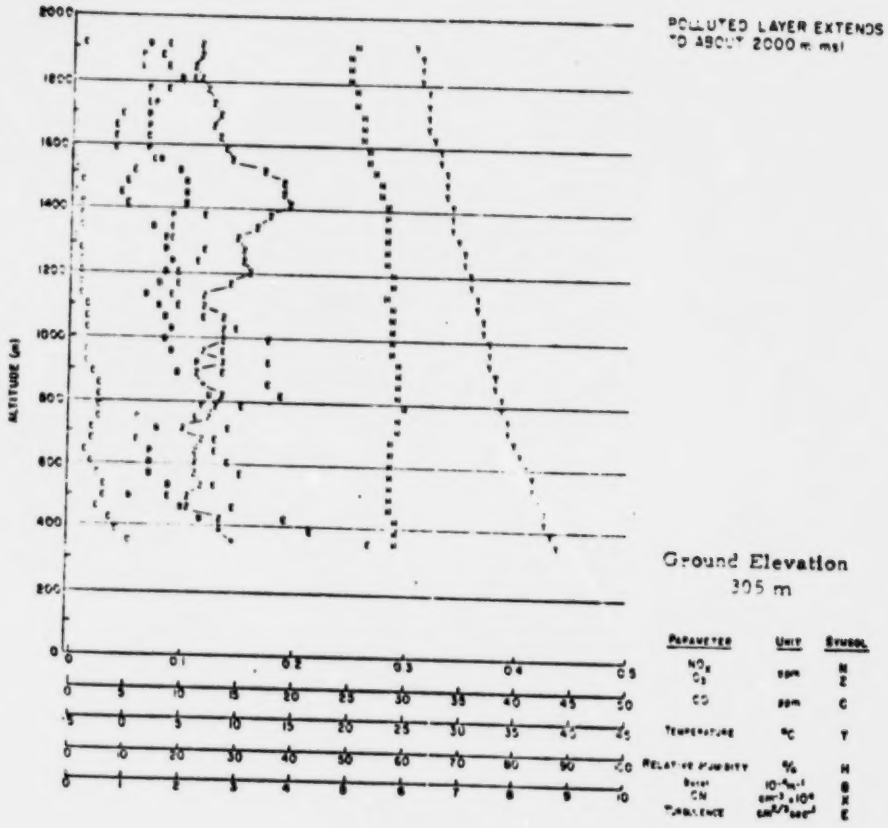


Fig. II-25. VERTICAL SOUNDING OVER BRACKETT (BRA) SEPTEMBER 21, 1972, 1625 PDT

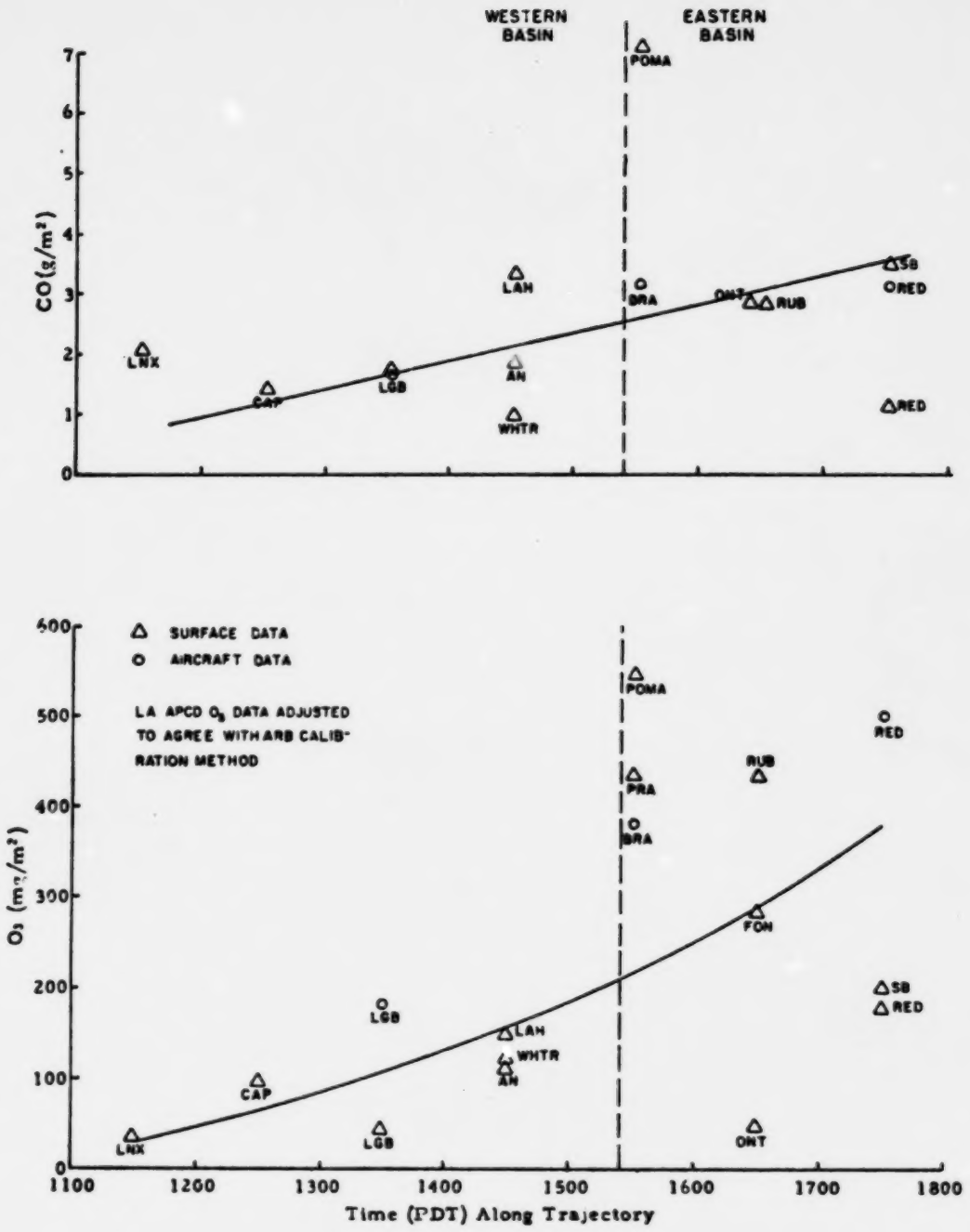


Fig. II-26. POLLUTANT LOADINGS IN SURFACE MIXED LAYER ALONG TRAJECTORY ARRIVING AT REDLANDS AT 1730 PDT, SEPTEMBER 21, 1972 (from aircraft measurements plus estimates made from ground data and mixing heights)

Figure II-26 shows that the CO loading of the air mass sampled in the afternoon sounding at Redlands increased as it passed over the western basin, from Long Beach to Brackett. Quantitative estimates of emissions based on the magnitude of this increase are probably unwarranted, as the data from the Long Beach sounding are somewhat noisy and the mixing layer structure in general was complicated and difficult to define precisely. Between Brackett and Redlands there was little apparent increase in the CO loading, although the vertical distribution of CO concentrations changed. At Brackett CO concentrations decreased markedly with height in the first few hundred meters, indicating recent emissions at ground level. This conclusion is backed up by the high ground level CO point at nearby Pomona (POMA). By the time the air mass had reached Redlands, CO concentrations in the first few hundred meters were virtually constant, indicating a much lower level of fresh emissions. These observations indicate that, as would be expected from a comparison of the emissions in Table II-1 with the trajectories in Fig. II-20, most of the CO in the air sampled at Redlands was emitted in the western basin.

Using CO as a tracer for ozone precursors which were not measured directly, as was done for July 25, 1973 we can deduce that a large fraction of the ozone precursors introduced into the air mass sampled at Redlands were emitted in the western basin.

The ozone loading increased between Long Beach and Brackett, and again between Brackett and Redlands. The ozone concentration over Redlands was nearly uniform with respect to height, indicating that the half-life of ozone due to scavenging by fresh emissions was relatively long. It appears likely, on the basis of the foregoing analysis, that most of the ozone measured at Redlands in the afternoon was produced in the western basin, or produced in the eastern basin from precursors emitted in the western basin, again evidence of the transport of ozone or ozone precursors from urban centers to surrounding areas.

B. Denver on November 21, 1973

An example of the transport of ozone and/or its precursors under conditions quite different from those in Los Angeles is provided by the data from a study conducted in the Denver, Colorado area on November 21, 1973 (Blumenthal et al., 1974). The distance over which the ozone and its precursors and tracers were observed to travel in this instance was small in comparison to the two Los Angeles cases just discussed (due to the size of the observing network) but the path and source of the pollutants is quite clear.

On the morning of November 21, 1973 an urban plume moved north from metropolitan Denver confined to a surface layer about 90 m (300 ft) deep. Between 0830 and 0930 MST, aircraft soundings at three locations north and northwest of Denver measured the vertical distribution of pollutants in the plume. After another hour of slow northward plume movement over a suburban area, all surface winds and low-level winds aloft shifted to easterly, driving the plume westward toward a rural lake, one of the sites of the morning soundings. A second aircraft sounding at the lake at 1130 MST confirms that the polluted air had, indeed, arrived over the lake site with little change in its primary pollutant burden, but a 100 percent increase in O_3 concentrations despite a three-fold increase in the depth of the mixing layer. At the same time, aircraft soundings at the other two sites show roughly clean air values for all measured pollutants.

The data available for November 21, 1973 in the Denver area were basically the same type of data acquired in the Los Angeles studies -- vertical soundings of air quality by aircraft, hourly winds aloft observations and hourly surface winds. Fig. II-27 shows the three locations where aircraft soundings were made at mid-morning and midday. These sities are numbered one through three. Sites 1, 4, and 5 in Fig. II-27a were ballon-launching sites for hourly winds aloft observations from 0900 MST on. The observed winds at these sites at 90 m (300 ft) were used to construct the trajectory shown except for the portion from 1030 to 1130 MST. That portion was constructed from the constant wind direction and the average speed from the surface to 270m (900 ft). Prior to 0830 MST, only surface winds were observed, and they proved to be light and variable with a slight tendency toward weak southerly.

In support of the calculated air trajectories, the Denver urban plume can be traced with NO_x, which is formed almost exclusively by combustion sources such as motor vehicles, power plants, and heating units. The six aircraft soundings are shown in Figs. II-28, 29, and 30. Figures II-27b and c show NO_x and O_3 concentrations integrated through the mixed layer for these soundings. On the morning set of soundings,

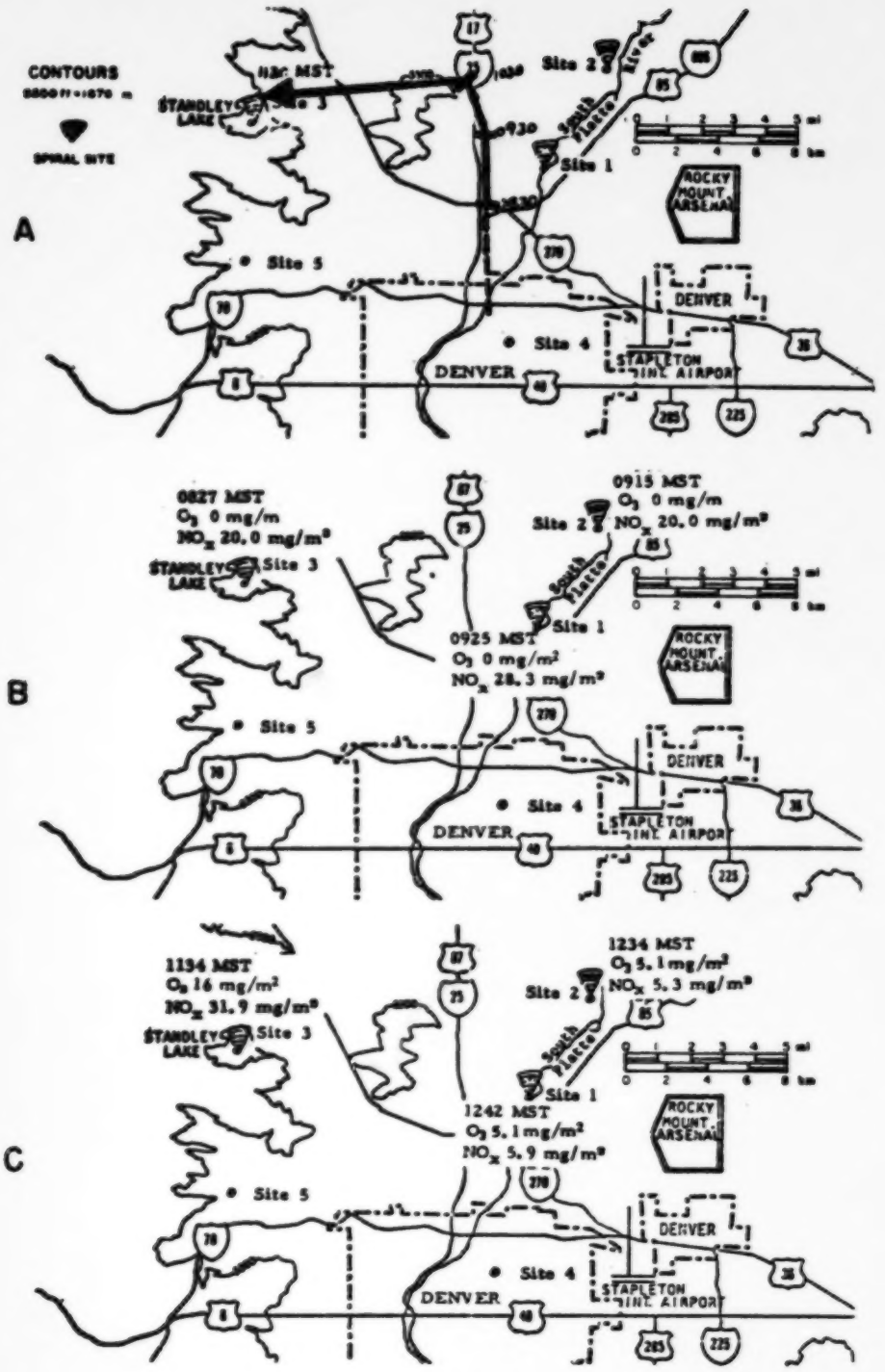


Fig. II-27. a. TRAJECTORY FOR AIR ARRIVING AT STANDLEY LAKE 1130 MST, 11/21/73
b. MORNING MIXING LAYER POLLUTANT DATA
c. MIDDAY MIXING LAYER POLLUTANT DATA

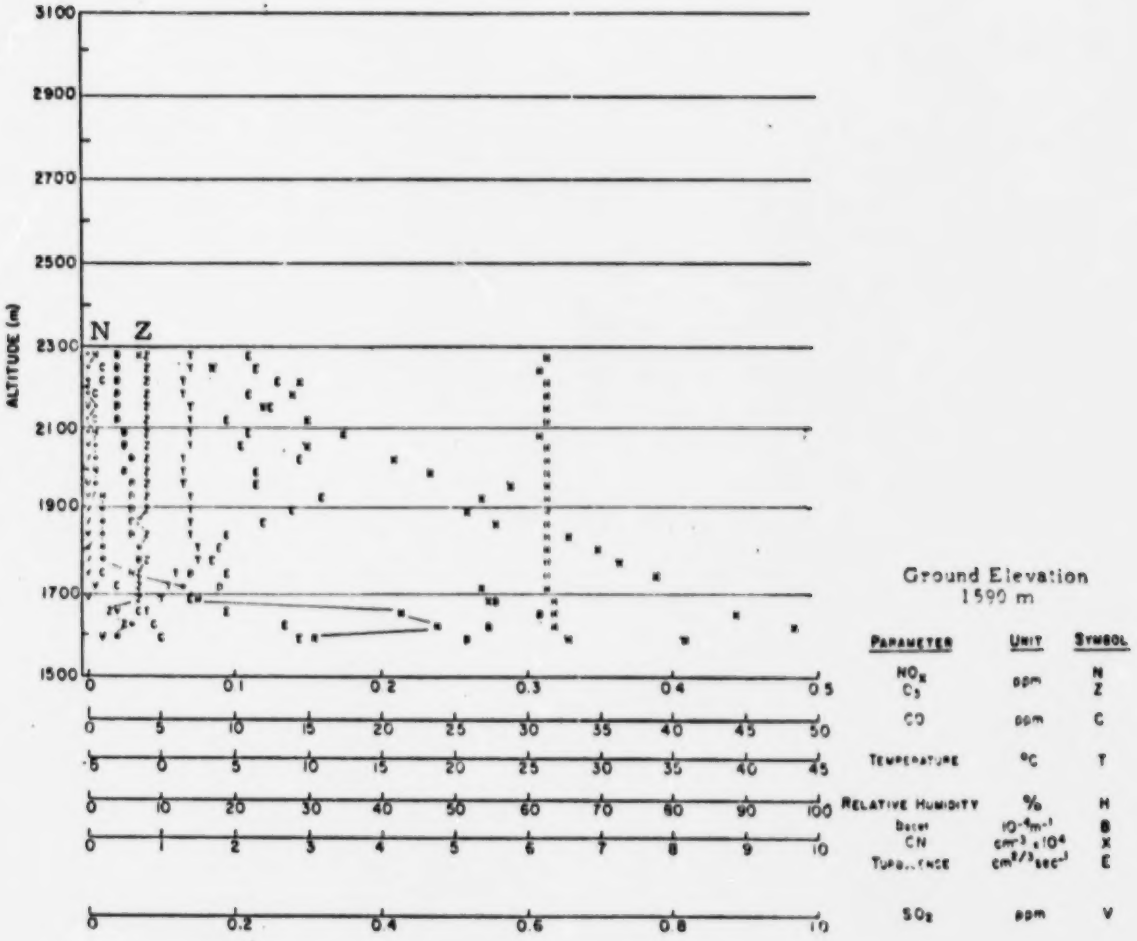


Fig. II-28a. VERTICAL PROFILES OVER EPA TRAILER (SITE 1) ON NOVEMBER 21, 1973, 0925 MST

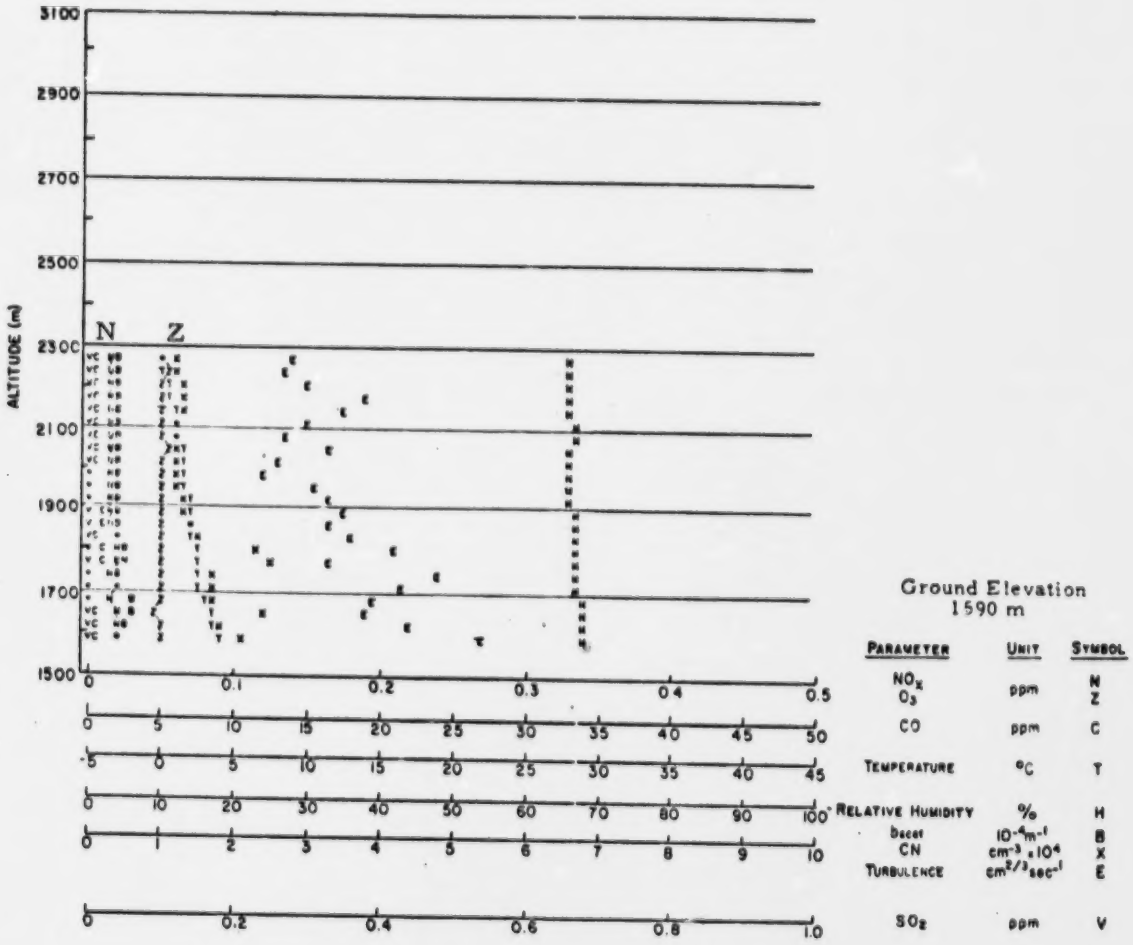


Fig. II-28b. VERTICAL PROFILES OVER EPA TRAILER (SITE 1) ON NOVEMBER 21, 1973, 1242 MST

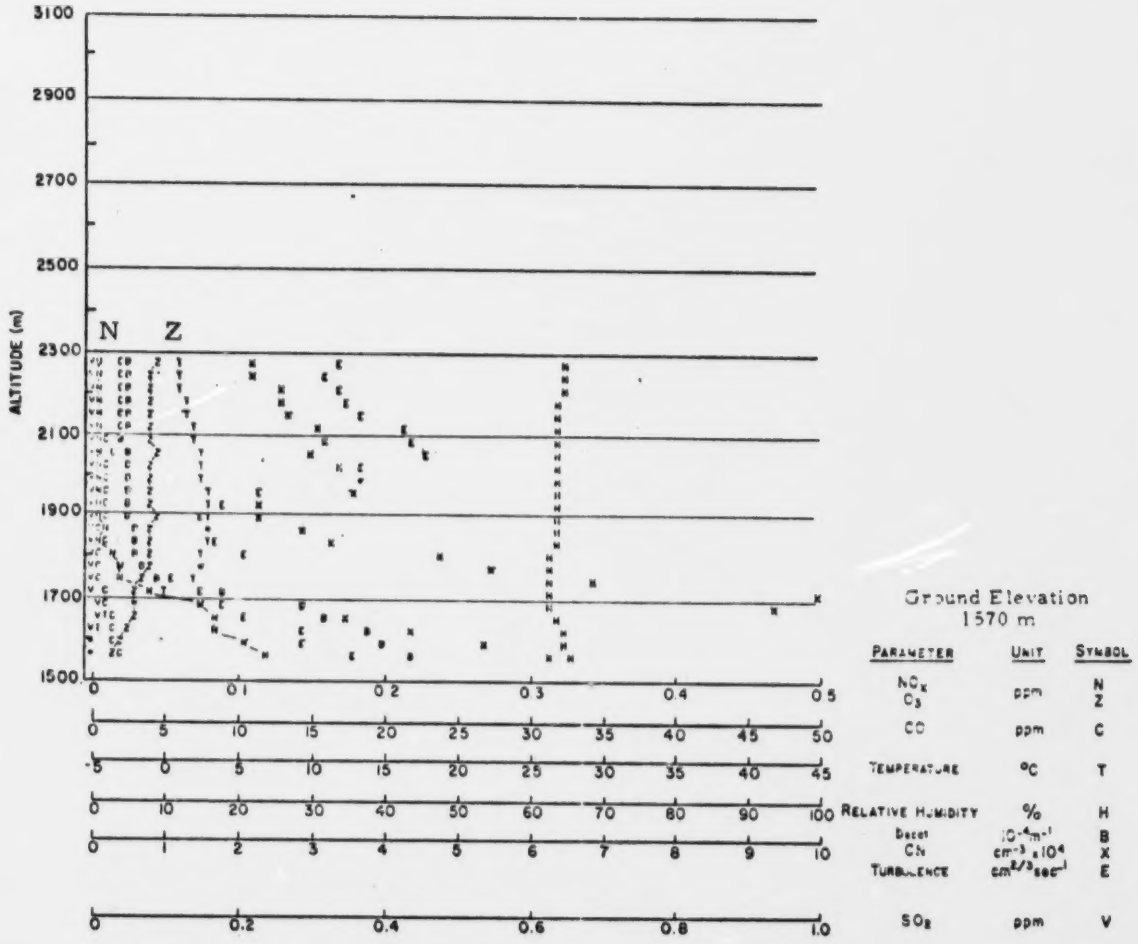


Fig. II-29a. VERTICAL PROFILES OVER HENDERSON (SITE 2) ON NOVEMBER 21, 1973, 0915 MST

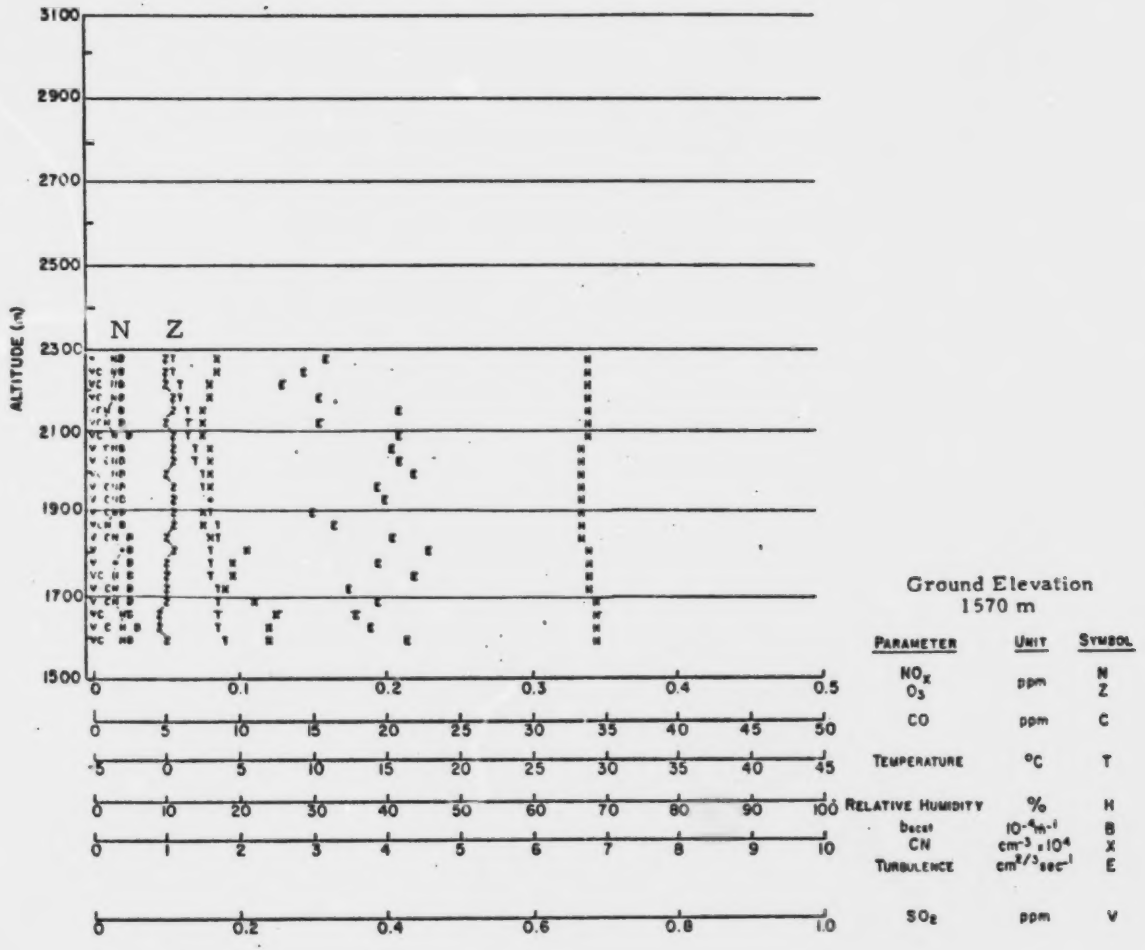


Fig. II-29b. VERTICAL PROFILES OVER HENDERSON (SITE 2) ON NOVEMBER 21, 1973, 1234 MST

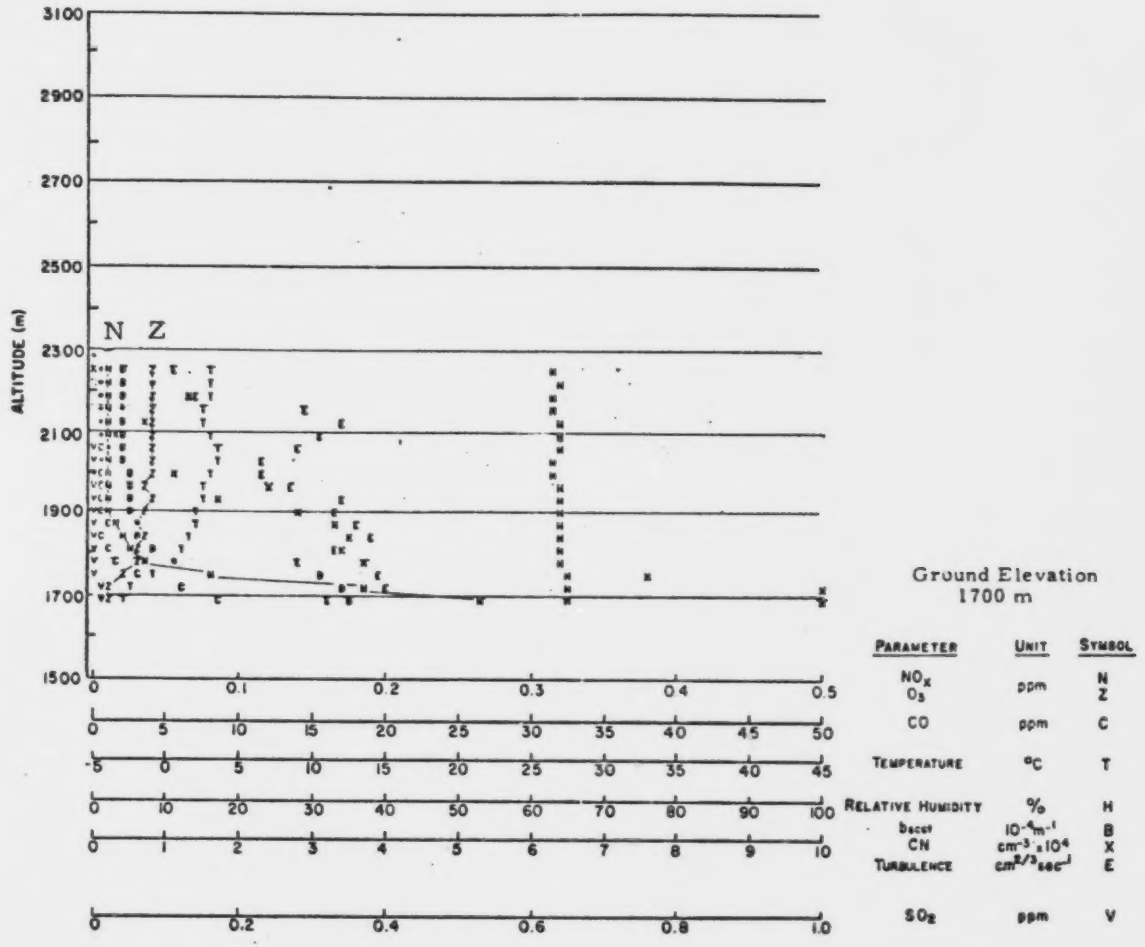


Fig. II-30a. VERTICAL PROFILES OVER STANDLEY LAKE (SITE 3) ON NOVEMBER 21, 1973, 0822 MST

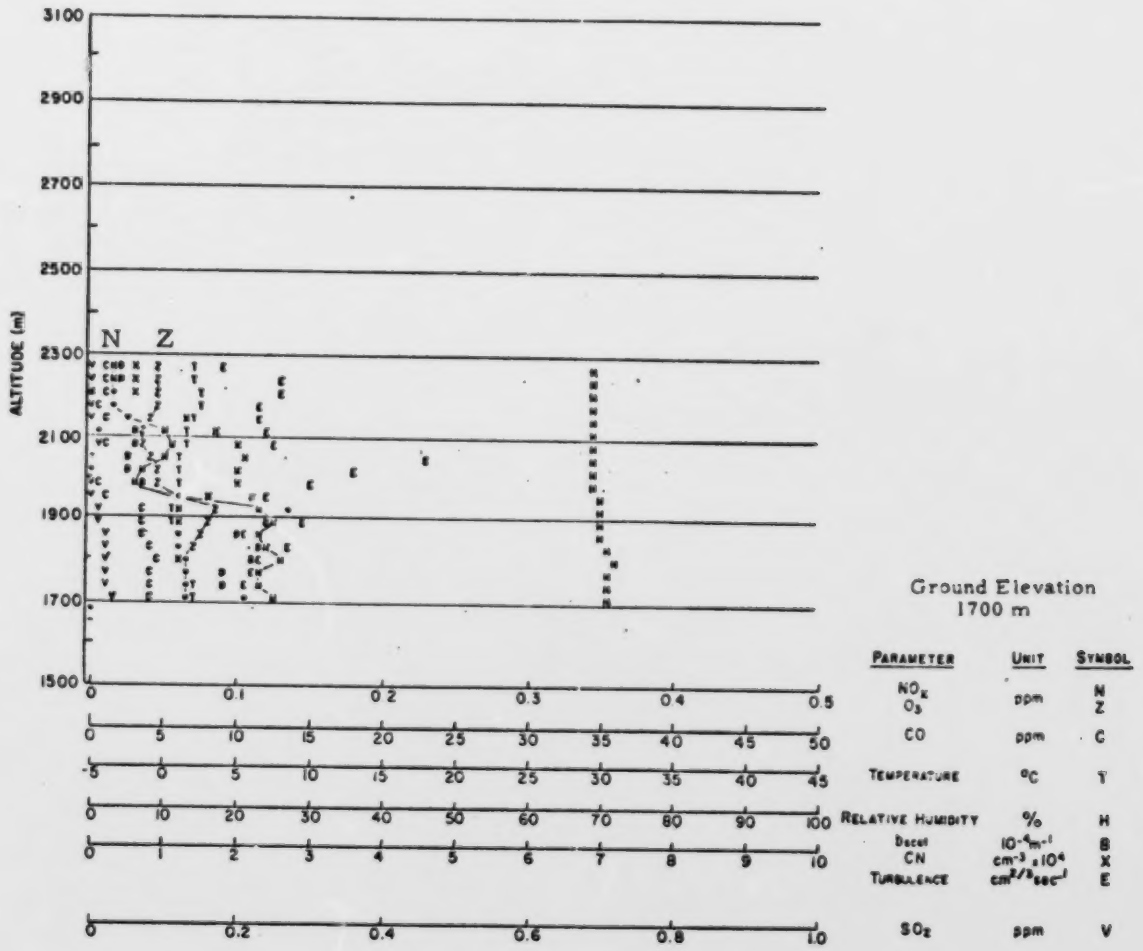


Fig. II-30b. VERTICAL PROFILES OVER STANDLEY LAKE (SITE 3) ON NOVEMBER 21, 1973, 1135 MST

all three sites showed modest NO_x totals (see Fig. II-27b). O_3 values in the lowest 90 meters (300 feet) or so are all below the background count of 4 pphm found at higher levels. (Integrations for ozone (L_x) have been corrected for a background level of 4 pphm. Negative values of the integral are listed in Fig. II-27 as zero).

At midday, when the trajectory shows that the surface layer of air which had been just west of site 1 at 0930 MST should be over Standley Lake, the only spiral showing a heavy load of NO_x is that over site 3 at Standley Lake. The O_3 and NO_x concentrations at both of the other sites are nearly at background levels despite the continued presence of a slightly stable lapse rate.

Comparisons of the data for Site 1 at 0930 MST and that for Site 3 at 1130 show that the total NO_x within the surface layer has remained essentially constant over the two hour track of about 16 km (10 mi). This indicates that there have been few new emissions en route. In the absence of scavenging by fresh emissions, O_3 concentrations have built up well above background levels, due to continuing photochemical reaction.

There is little doubt from the evidence presented that the air over rural Standley Lake at 1130 acquired its ozone precursors earlier over Denver, even though the ozone itself did not form until after the air passed site number 1 at 0930 MST. This is a very similar situation to that observed over and downwind from Los Angeles.

A more detailed discussion of the aging of the polluted air mass en route to Standley Lake is given in the paper by Blumenthal et al. included as Appendix B.

III. OZONE IN RURAL AREAS

Ozone has frequently been observed in rural areas remote from the nearest urban complex. Several authors, such as Miller, McCutchan and Milligan (1972), Edinger at al., (1972) and Miller and Ahrens (1970) have tried, with varying degrees of success, to relate the ozone to some urban source. Such a relationship is supported by the foregoing demonstration that ozone and/or its precursors can be transported relatively long distances. Several cases of rural ozone of apparent urban origin have also been noted in recent MRI studies. The following sections are devoted to two of these cases.

The studies discussed here consisted of special aircraft pollution observations made over remote mountain and desert locations, together with observations in the Riverside-San Bernardino air basin on two August days in 1973. Of particular significance were the measurements made over Lake Arrowhead and Hesperia (Fig. III-1). Lake Arrowhead is a mountain resort 21 km northeast of San Bernardino at 1560 m (5110 ft) msl. It is surrounded by national forest for 16 km (10 mi) or more in all directions and is about 1 km above the valley to the west. There is little or no industry and little traffic in the area. A single secondary road encircles the lake and a second road passes the lake about 2 km to the south. Hesperia is located in the desert about 30 km north of San Bernardino at an elevation of 1035 m msl on the north slope of the mountain ridge which includes Lake Arrowhead.

The aircraft sampling spirals on the two days of interest were conducted over a small airport north of the lake (ARR), at Hesperia (HES), and in the eastern portion of the LA basin. Winds were observed every two hours at Strawberry Mountain Lookout southwest of the lake, and the Air Pollution Research Center of the University of California at Riverside made hourly observations of wind, temperature, and oxidant at the Skyforest Ranger Station along the highway south of Lake Arrowhead.

A. August 16, 1973, Arrowhead and Hesperia

August 16, 1973 was a day of moderate smog in the Riverside-San Bernardino air basin, with ozone values in excess of 30 pphm observed by aircraft. The day began with surface oxidant concentrations at Skyforest near background levels (Fig. III-2), indicating an absence of local pollution sources. Surface winds at both Skyforest and Strawberrry Mountain were northerly all night, bringing in air from the forest, mountains, and desert to the north of Lake Arrowhead. Fig. III-3 shows the morning sounding made at 0939 PDT over Lake Arrowhead. This sounding shows clean air with nitrogen oxides, ozone, and b_{scat} at or near background.

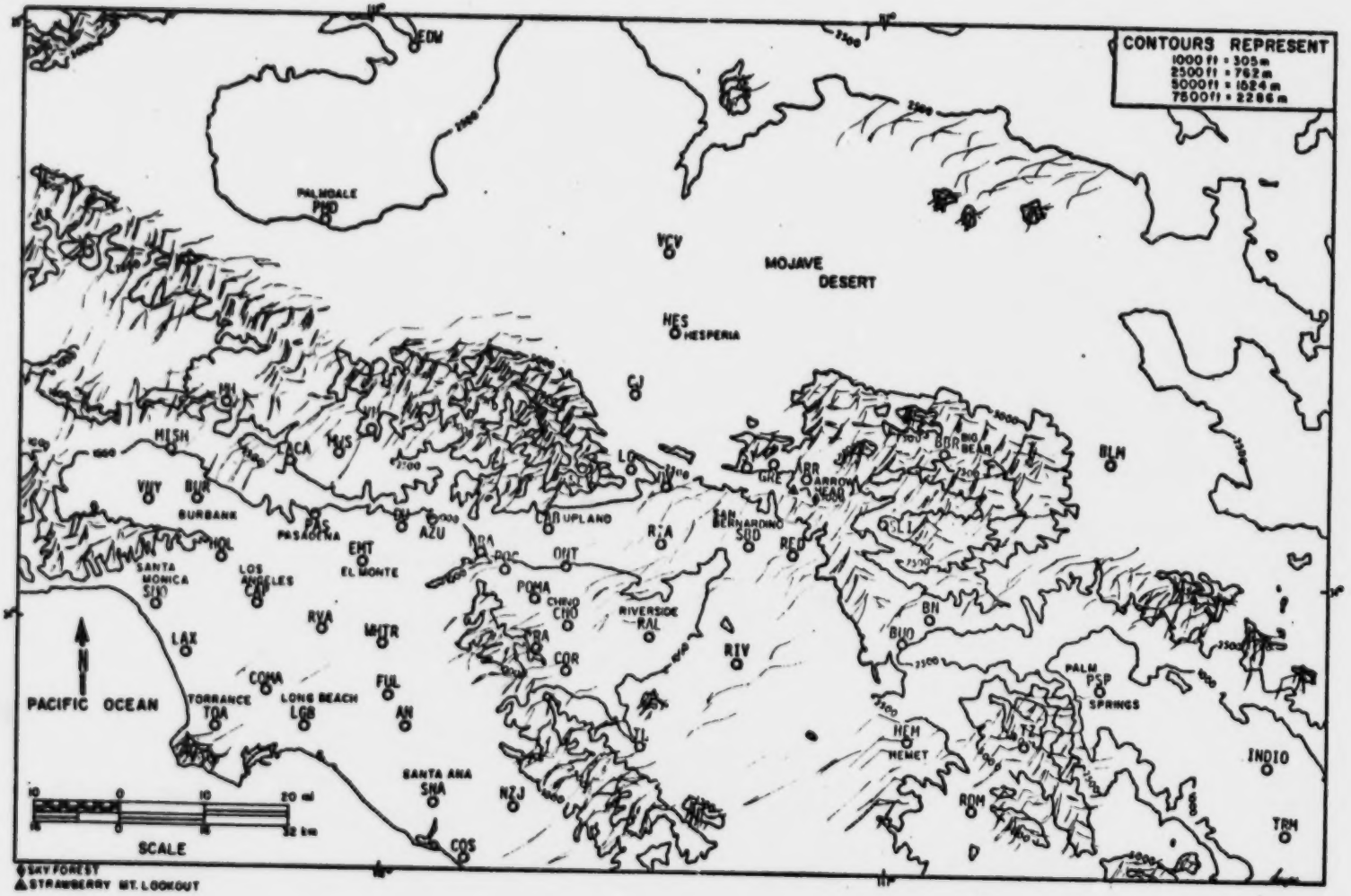


Fig. III-1. LOS ANGELES BASIN AND SURROUNDING AREAS

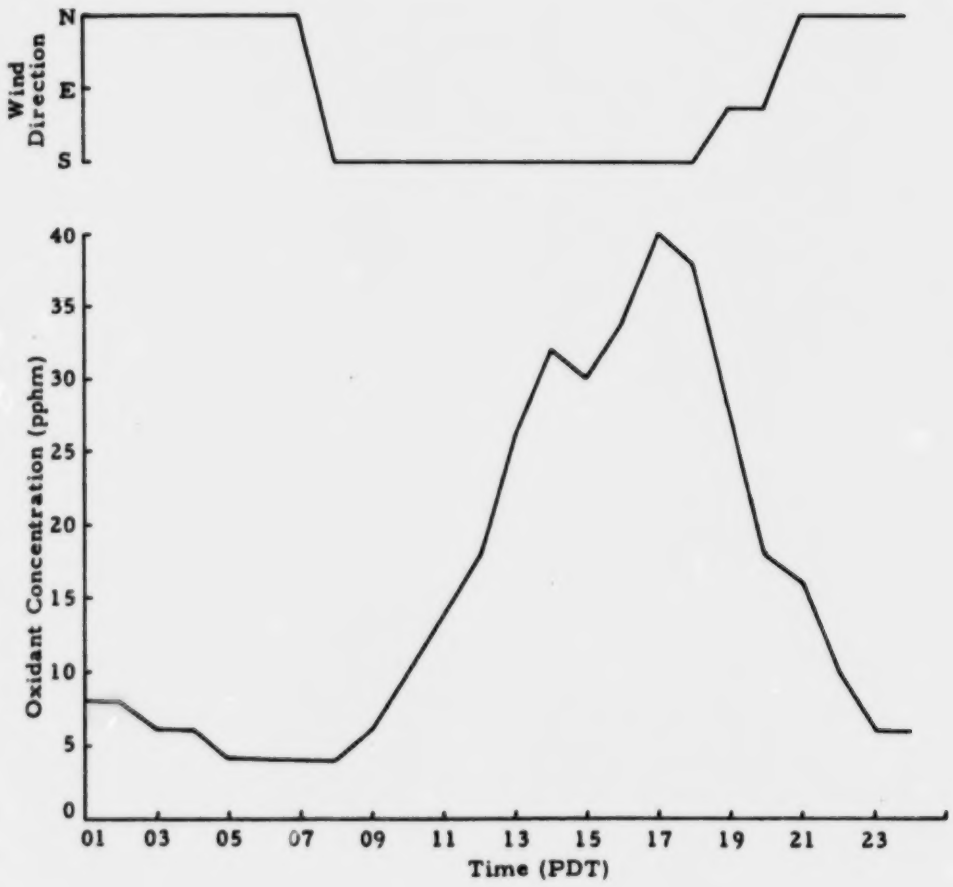


Fig. III-2. HOURLY AVERAGE OXIDANT CONCENTRATIONS AND SURFACE WINDS MEASURED AT SKYFOREST RANGER STATION, AUGUST 16, 1973

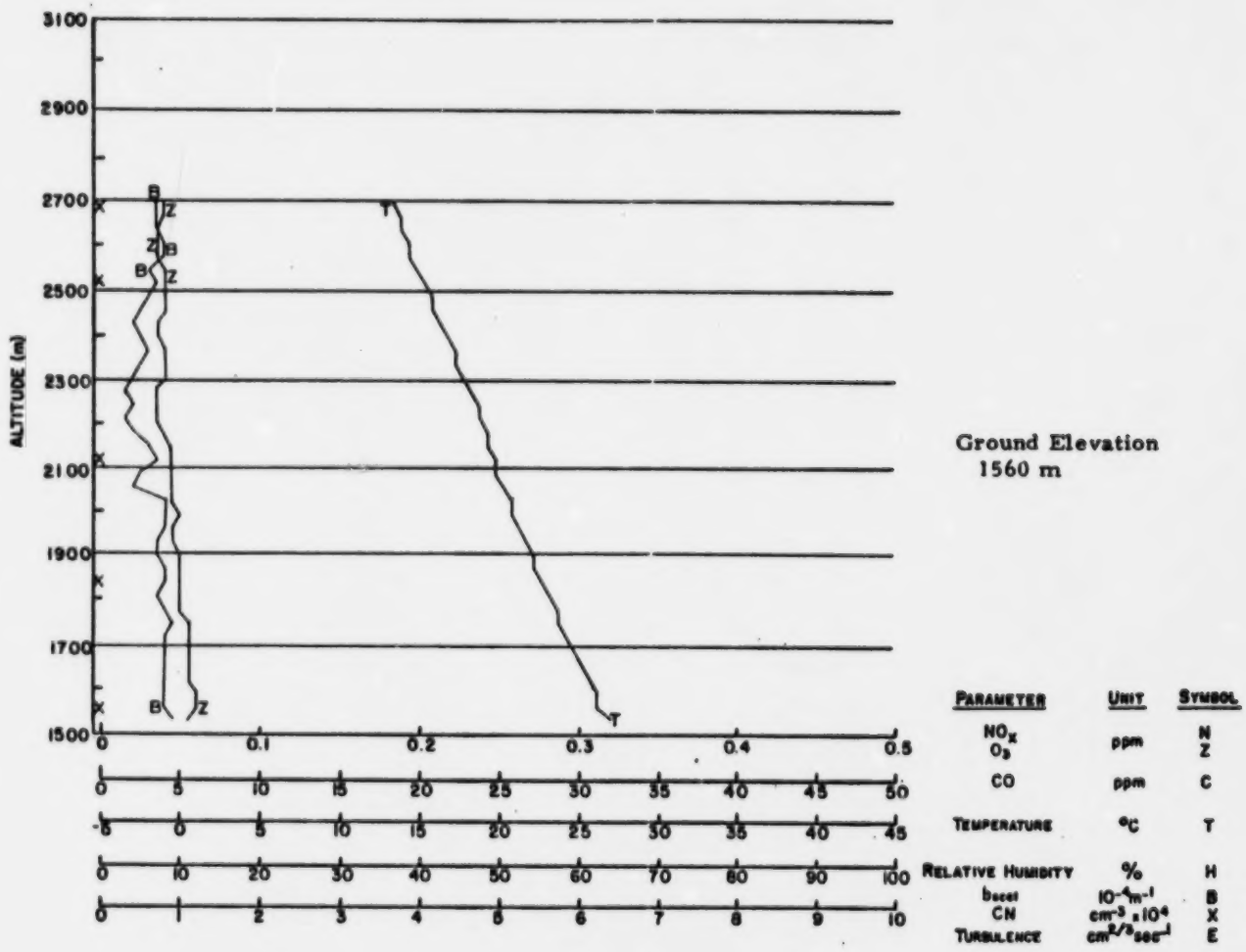


Fig. III-3. VERTICAL PROFILE OVER ARROWHEAD (ARR)
AUGUST 16, 1973, 0939 PDT

By the time the afternoon Lake Arrowhead sounding was made at 1645 PDT, conditions had changed considerably with ozone and b_{scat} showing moderately high values in the lower 300 m (900 ft) for such a remote, rural area. This sounding is given in Fig. III-4, where two features are of special interest. First, the increase in ozone and b_{scat} are confined to the layer below 1900 m (6300 ft) msl, and second, the ozone and b_{scat} are well correlated in this layer while the condensation nuclei count is quite low. The low ozone level at the top of the sounding (above 6300 ft) suggests that the ozone did not descend from higher altitudes. Furthermore, the high correlation between b_{scat} and ozone and the absence of condensation nuclei within the pollution layer indicate a well-aged polluted air mass, devoid of fresh emissions. While the aircraft at Lake Arrowhead was measuring ozone concentrations of 0.10 - 0.13 ppm, the Skyforest Ranger Station was recording a one-hour average oxidant concentration of 0.40 ppm. The difference in these concentrations is attributed primarily to the fact that the Ranger Station was situated just below the crest of the mountains bordering the Riverside-San Bernardino Air Basin, several miles upwind of Lake Arrowhead airport.

The above observations strongly suggest that the ozone is ground-based and that the ozone precursors were not of local origin. The surface winds at Skyforest ranged from 8 to 13 km/hr (5 to 7 mph) and those at Strawberry Mountain about 11 to 22 km/hr (6 to 12 mph) for the 7-hour period between the two soundings. Under these conditions, the aged pollution would have entered the atmosphere somewhere upwind of the forest, which the air traverses in less than two hours.

A similar sequence of events is shown in Figs. III-5 and III-6 which represent soundings made at 0904 PDT and 1656 PDT at Hesperia. Figure III-5 shows relatively clean air at all levels on the morning sounding while Fig. III-6 indicates that ozone and b_{scat} values have increased substantially in the lowest 460 m (1500 ft) by the late afternoon. Again, the ozone and b_{scat} profiles are well correlated while the lack of condensation nuclei indicates aged pollution.

The streamline pattern for 1600 PDT is shown in Fig. III-7. The San Bernardino winds aloft in Fig. III-7 show that air over Lake Arrowhead and Hesperia has a previous trajectory over San Bernardino or Rialto. Fig. III-7 shows one streamline passing through Cajon Pass (from RIA to HES) which represents a typical exit route for air leaving the Los Angeles Basin. The figure also shows clearly the wind flow pattern up the heated slopes east of Cajon Pass (near SBD and RED) which is characteristic of the mountain slopes along the north and east portions of the basin during the afternoon. With the observed wind velocities of 10 to 20 km/hr (see pibal summary, Table III-1), air

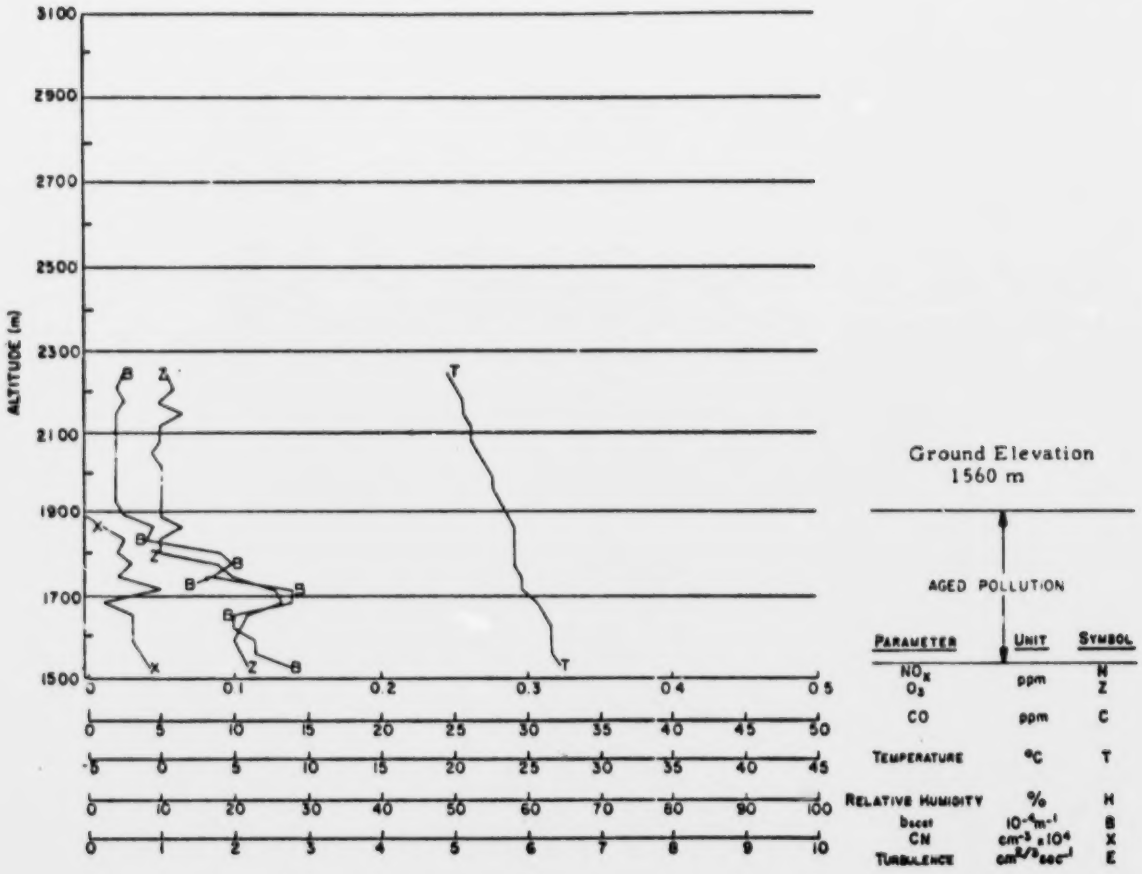


Fig. III-4. VERTICAL PROFILE OVER ARROWHEAD (ARR)
AUGUST 16, 1973, 1645 PDT

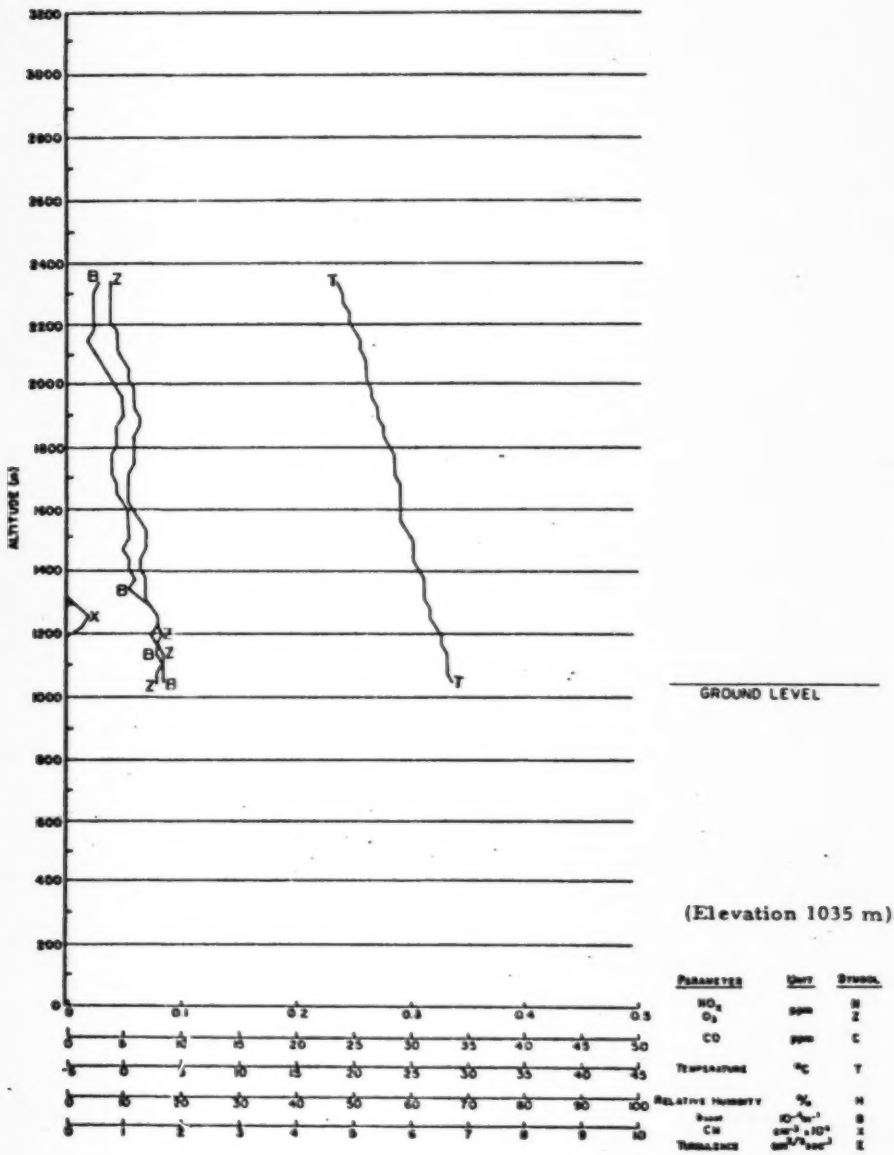


Fig. III-5. VERTICAL PROFILE OVER HESPERIA (HES) AUGUST 16, 1973, 0904 PDT

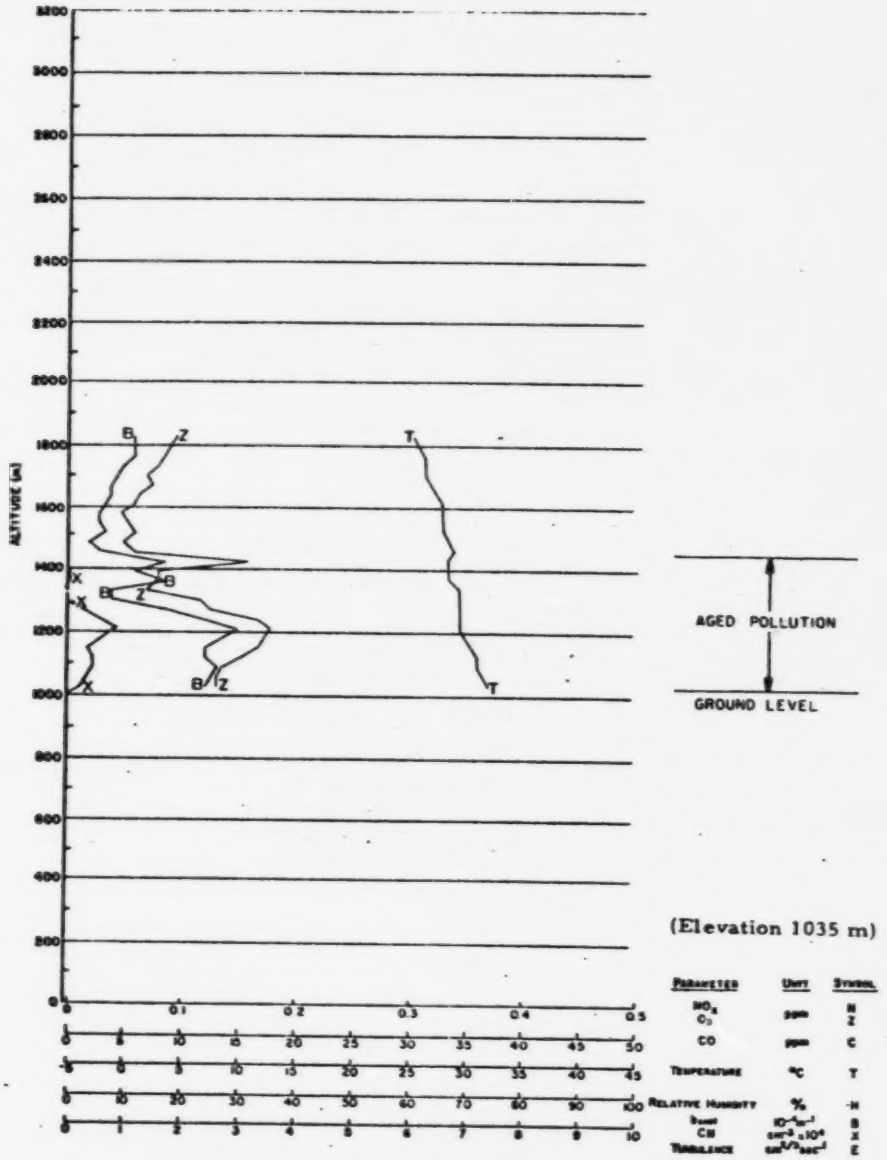
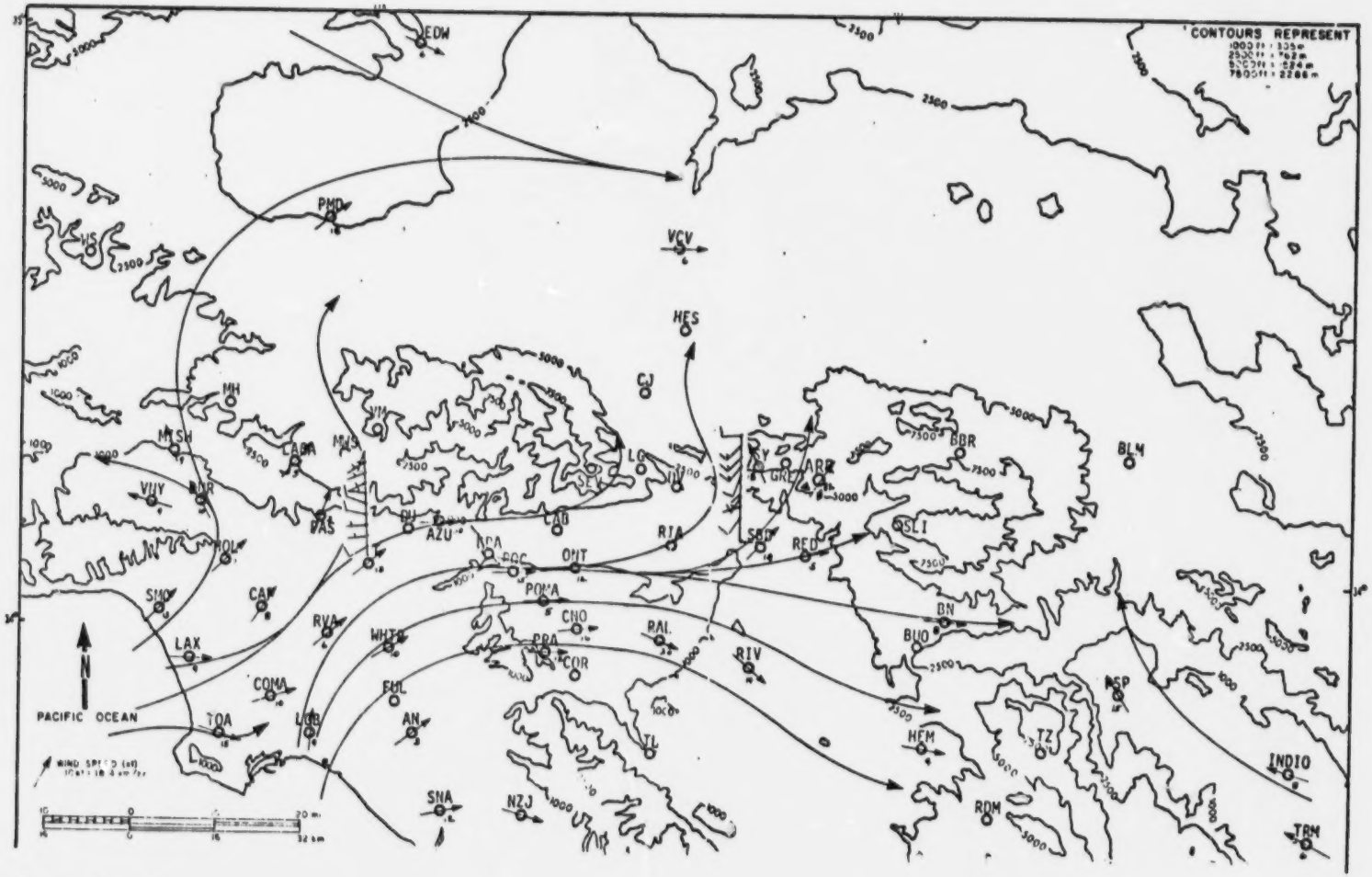


Fig. III-6. VERTICAL PROFILE OVER HESPERIA (HES) AUGUST 16, 1973, 1656 PDT



♦ Skyforest
▲ Strawberry Mt. Lookout

Fig. III-7. STREAMLINES FOR 1600 PDT on 8/16/73

TABLE III-1

AUGUST 16, 1973 PIBAL DATA

Height	WD	WS(km/hr)
LAX - 1230 PDT		
Sfc	250	18
1000	220	13
2000	250	7
3000	225	4
4000	290	11
6000	320	15
7000	320	7
8000	0	0
SBD - 1320 PDT		
2000	230	13
3000	255	9
4000	225	7
5000	200	9
6000	190	11
7000	225	17
8000	220	22
9000	230	11
SBD - 1615 PDT		
Sfc	240	9
2000	210	18
3000	255	9
4000	210	7
5000	180	17
6000	200	22
7000	215	30
8000	220	24
9000	225	28
10,000	260	15

Height	WD	WS(km/hr)
EMT - 1332 PDT		
Sfc	230	17
1000	225	18
2000	290	9
3000	240	7
4000	280	17
5000	315	15
6000	295	7
7000	265	7
8000	245	9
9000	245	13
10,000	200	7
11,000	215	15
EMT - 1520 PDT		
Sfc	240	17
1000	240	17
2000	260	11
3000	265	9
4000	285	19
5000	295	15
6000	280	9
7000	240	6
8000	250	13
9000	240	11
10,000	205	7
11,000	235	15
12,000	230	22

arriving at Arrowhead or Hesperia around 1600 PDT should have passed over the San Bernardino, Rialto area one to two hours previously.

Figures III-8 and III-9 show vertical soundings made at Rialto and Redlands at 1337 PDT and 1317 PDT, respectively. The soundings show a polluted layer of about 760 m depth (2500 ft) at both locations. High values of both ozone and b_{scat} are observed in the layer which indicate the generally aged nature of the pollution. Some evidence of fresh emissions is shown by the moderate level of condensation nuclei, but there was insufficient NO production locally to reduce the ozone values substantially.

The foregoing data indicate that the polluted layer observed near Rialto and Redlands moved upslope to the Lake Arrowhead area and through Cajon Pass to Hesperia by late afternoon. b_{scat} and ozone values are reduced in nearly a proportionate manner during this travel period due mainly to dilution with cleaner air. At the same time, the condensation nuclei, in both cases, decreased markedly as the aging process of coagulation with larger aerosols occurred.

This sequence of events is further supported by surface oxidant measurements which show a peak value at San Bernardino at 1500 PDT and a peak at Skyforest at 1700 PDT. This difference in peak times is most readily accounted for by a simple transport of an air mass containing ozone or precursors from San Bernardino to Skyforest.

The streamline pattern shown in Fig. III-7 was established about 1000 PDT and continued through 1900 with little change in directional characteristics. As indicated in an earlier chapter, the most probable source of the air contributing to the 1500 PDT peak at San Bernardino is the central Los Angeles area from which the air parcels, stagnating in the early morning hours, begin to move at about 1000 PDT along the indicated streamlines into the Rialto-San Bernardino area.

B. Lake Arrowhead on August 24, 1973

Conditions on August 24 were similar to those on the 16th. Figure III-10 shows the hourly oxidant concentrations recorded at the Skyforest Ranger Station. Figures III-11 and III-12 show the morning sounding in clean air over Lake Arrowhead and an afternoon sounding with high ozone and b_{scat} levels in the lowest 500 m. The surface winds at Strawberry Mountain, San Bernardino, and Riverside were southwesterly at 11 to 40 km/hr all day and winds aloft at San Bernardino and Banning were south to west at almost all levels and all four observational times (see Table III-2). Surface winds at Skyforest were not measured.

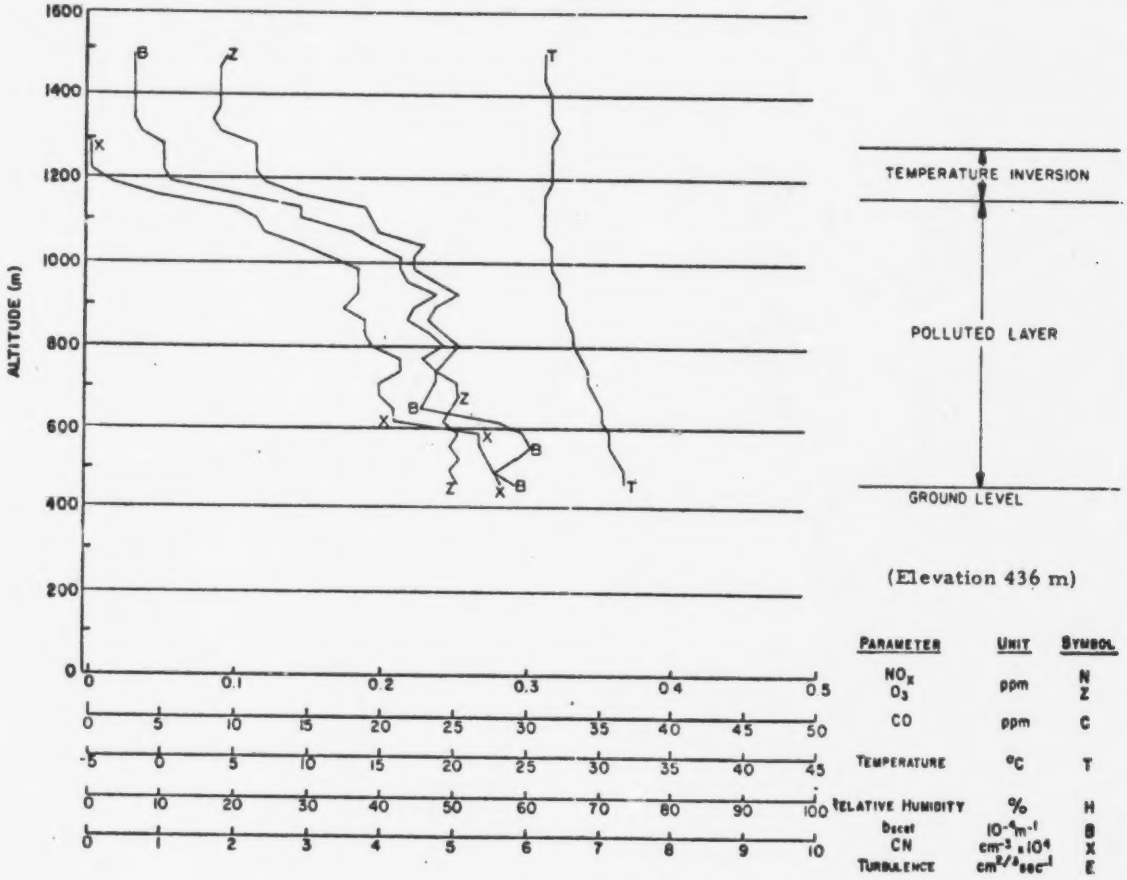


Fig. III-8. VERTICAL PROFILE OVER RIALTO (RIA)
AUGUST 16, 1973, 1337 PDT

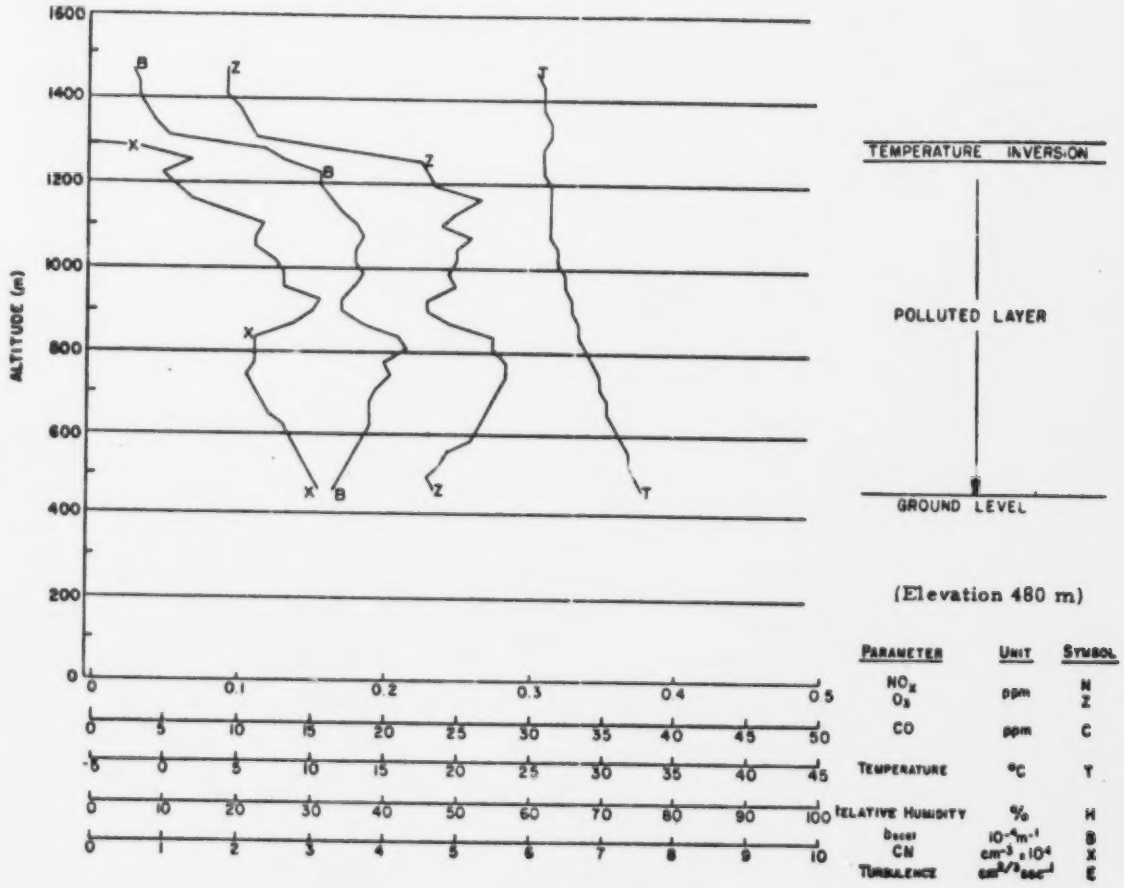


Fig. III-9. VERTICAL PROFILE OVER REDLANDS (RED)
AUGUST 16, 1973, 1317 PDT

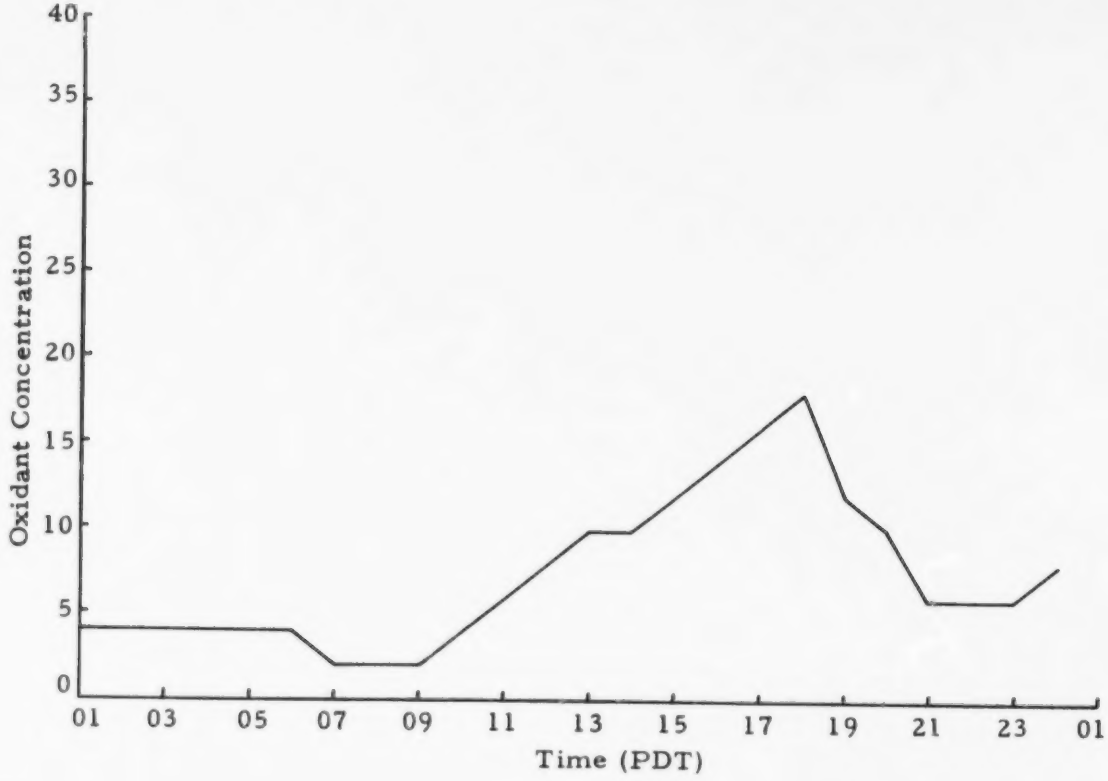


Fig. III-10. HOURLY AVERAGE OXIDANT CONCENTRATIONS MEASURED AT SKYFOREST RANGER STATION, AUGUST 24, 1973

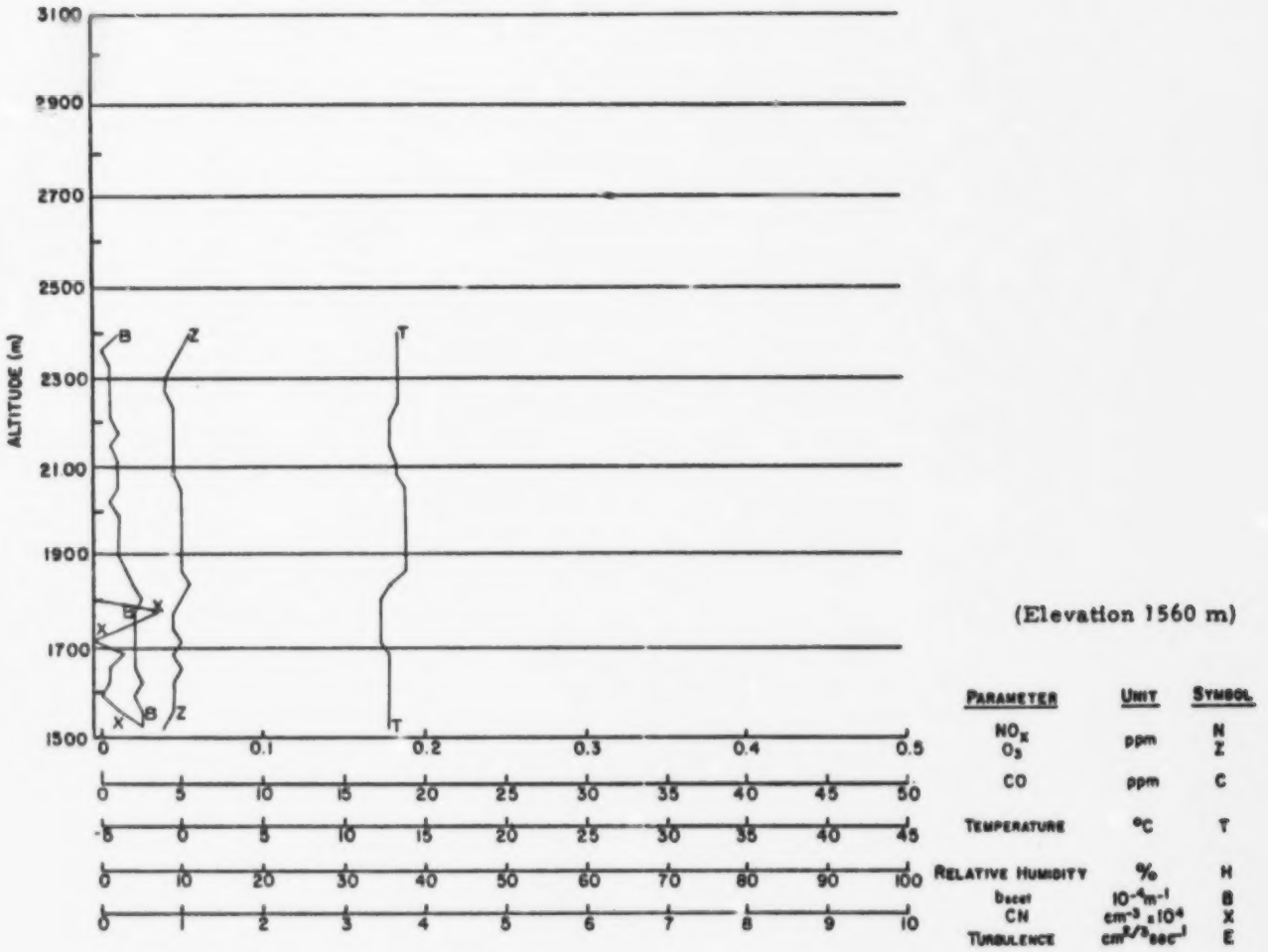


Fig. III-11. VERTICAL PROFILE OVER ARROWHEAD (ARR)
AUGUST 24, 1973, 0842 PDT

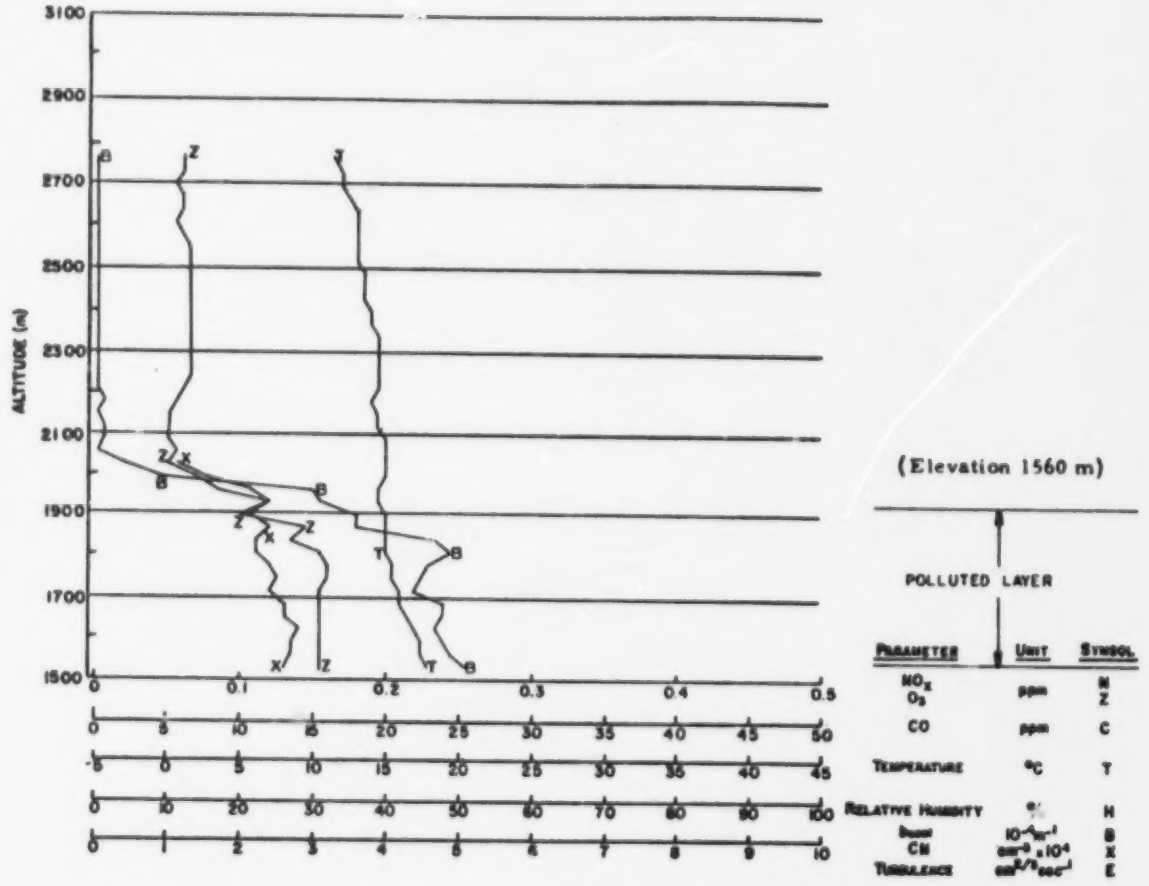


Fig. III-12. VERTICAL PROFILE OVER ARROWHEAD (ARR)
AUGUST 24, 1973, 1530 PDT

TABLE III-2

AUGUST 24, 1973 PIBAL DATA

Height	WD	WS(km/hr
BAN - 1000 PDT		
Sfc	280	22
3000	270	41
4000	250	17
5000	220	15
6000	170	13
7000	180	15
8000	210	26
9000	240	24
1000	250	22
BAN - 1200 PDT		
Sfc	280	24
3000	250	30
4000	250	31
5000	210	28
6000	160	17
7000	190	13
8000	200	20
9000	210	26
10,000	220	24
LAX - 1230 PDT		
Sfc	260	17
1000	250	9
2000	85	7
3000	110	7
4000	75	7
6000	105	9
7000	120	7
8000	235	9
9000	280	18
10,000	265	13

Height	WD	WS(km/hr
EMT - 1332 PDT		
Sfc	250	11
1000	235	15
2000	230	7
3000	195	6
4000	115	9
5000	105	17
6000	90	17
7000	110	11
8000	235	9
9000	245	9
10,000	245	18
11,000	245	9
SBD - 1345 PDT		
2000	245	15
3000	235	20
4000	230	7
5000	160	11
6000	145	17
7000	155	24
8000	190	26
BAN - 1400 PDT		
Sfc	270	22
3000	260	39
4000	270	30
5000	250	30
6000	200	33
7000	240	15
8000	230	26
9000	230	32
10,000	220	33

TABLE III-2
AUGUST 24, 1973 PIBAL DATA (Continued)

Height	WD	WD(km/hr
BAN - 1600 PDT		
Sfc		
3000	250	31
4000	260	46
5000	260	31
6000	260	22
7000	220	9
8000	240	22
9000	230	26
10,000	220	31

A similar sounding pattern is shown in Figs. III-13 and III-14 which give morning and afternoon soundings at Hesperia. The primary difference between the data for August 16 and 24 is the occurrence of moderate values of condensation nuclei at both Lake Arrowhead and Hesperia during the late afternoon.

The streamline pattern for 1600 PDT on August 24 is shown in Fig. III-15. The pattern is essentially the same as shown in Fig. III-7 for August 16. Flow through Cajon Pass toward Hesperia and up the heated slopes toward Lake Arrowhead is clearly indicated. This pattern was also established by 1000 PDT and continued with little change until 1900 PDT.

The flow pattern shown in Fig. III-15, together with the observed winds, indicate that the air passing over Arrowhead and Hesperia had a previous trajectory over the San Bernardino, Rialto, and Upland (CAB) area about 1-2 hours earlier. Figures III-16 and III-17 show the aircraft soundings made at CAB and Rialto at 1208 and 1321 PDT, respectively. CAB shows a well-mixed layer to 670 m (2200 ft) above ground level while Rialto shows mixing to 1070 m (3500 ft) above ground. Subsequent soundings in these areas showed even larger mixing depths by late afternoon. Both soundings show high ozone, high b_{scat}, and moderate condensation nuclei characteristics indicative of aged pollution, but with some fresh emissions.

Comparisons of the ozone and b_{scat} values at Hesperia and Arrowhead (Figs. III-12 to III-14) with the earlier soundings at Upland and Rialto (Figs. III-16, III-17) indicate slightly reduced values at Hesperia and Arrowhead. Again, the ozone and b_{scat} values tend to be proportionately similar, although some reduction in ozone values at Arrowhead appears to have occurred (Fig. III-12) relative to the b_{scat} values. It is suggested that the primary changes in ozone and b_{scat} values occurred as a result of dilution with cleaner air.

The trajectory of the polluted air from near Rialto to Arrowhead is further supported by peak times of surface oxidant values. On August 24, peak concentrations occurred at 1600 PDT at San Bernardino and at 1800 PDT at Skyforest. The relatively late time of the peak occurrence at Skyforest argues rather strongly against any local generation of the oxidant.

As discussed earlier, the trajectories of the air at Upland and Rialto can be traced back to the central Los Angeles area along the streamlines shown in Fig. III-15. Air parcels arriving at the peak oxidant period in the San Bernardino area are likely to have originated

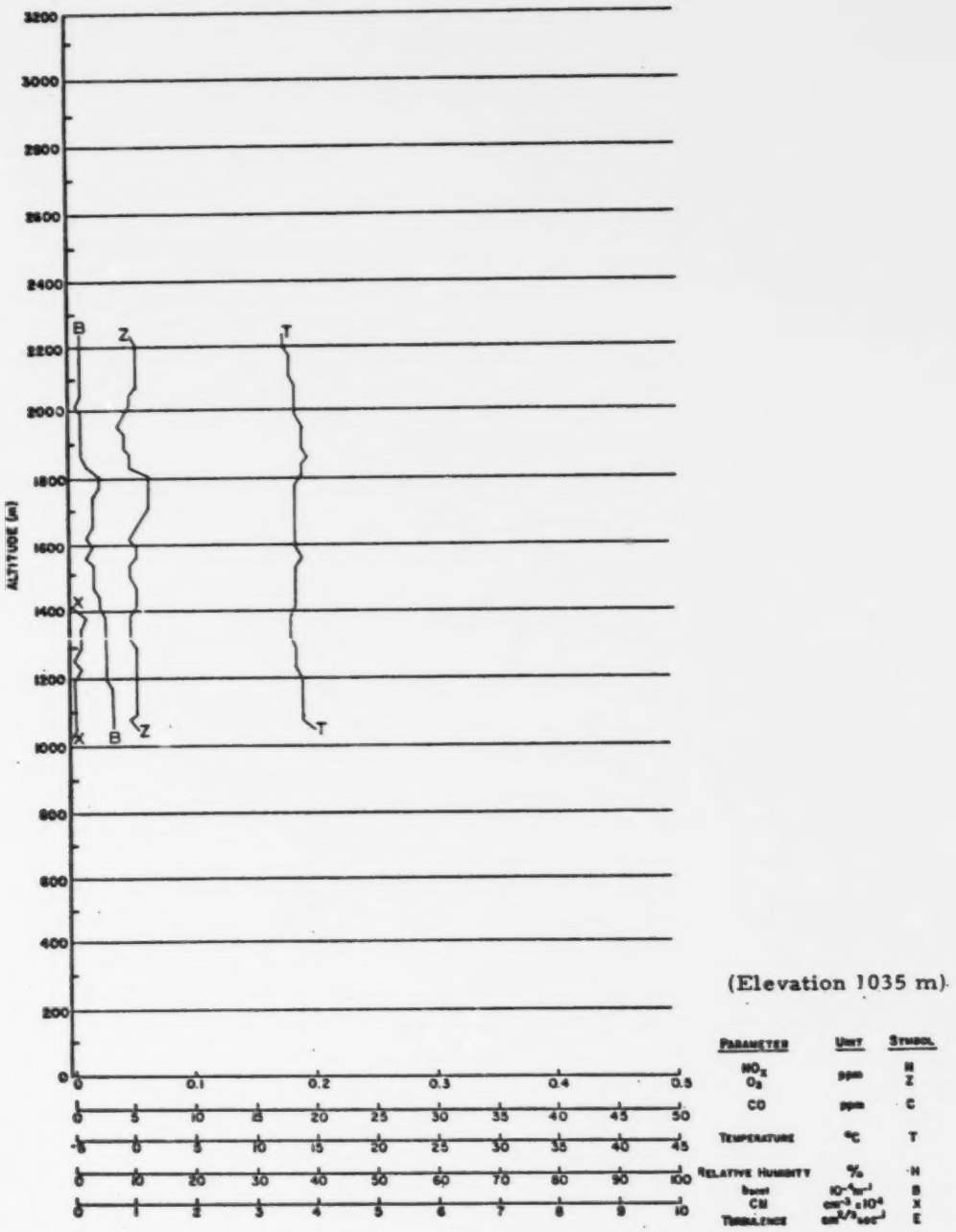


Fig. III-13. VERTICAL PROFILE OVER HESPERIA (HES)
AUGUST 24, 1973, 0831 PDT

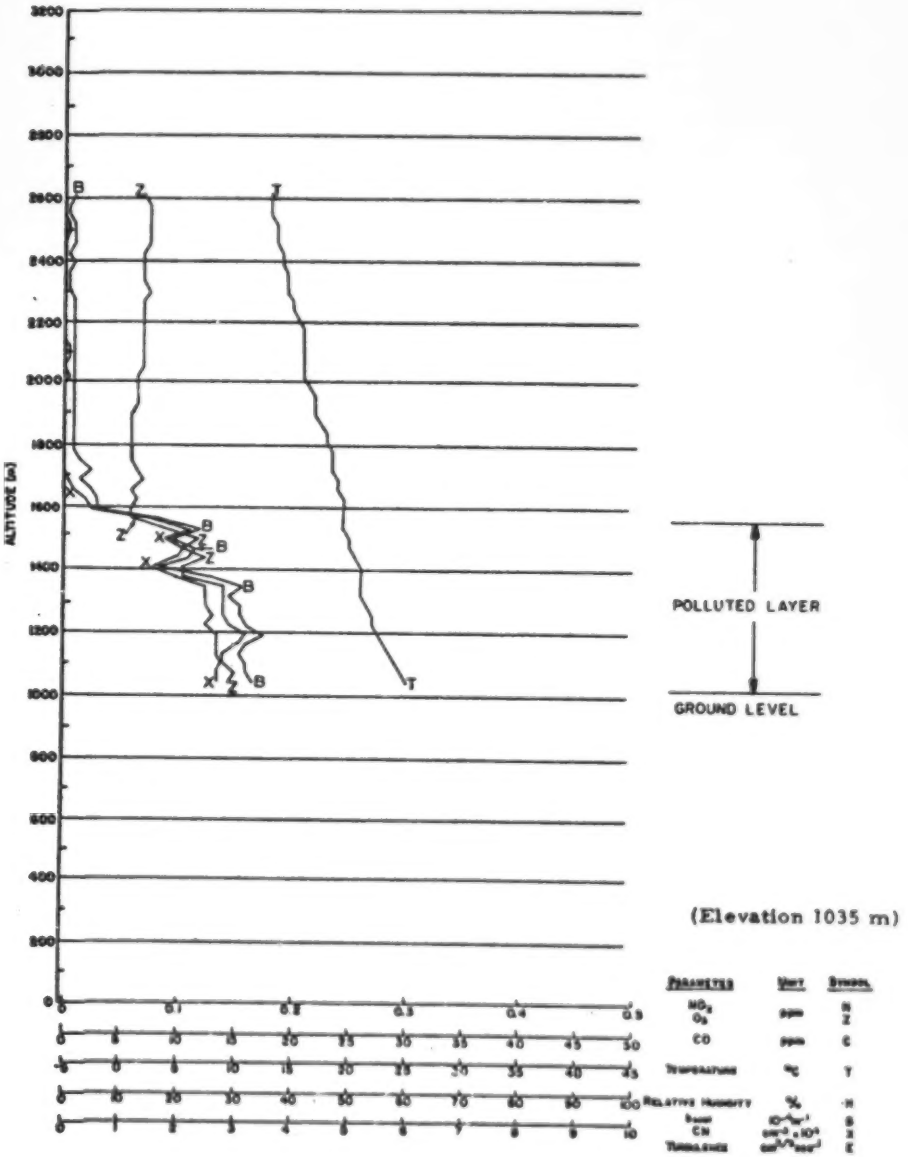
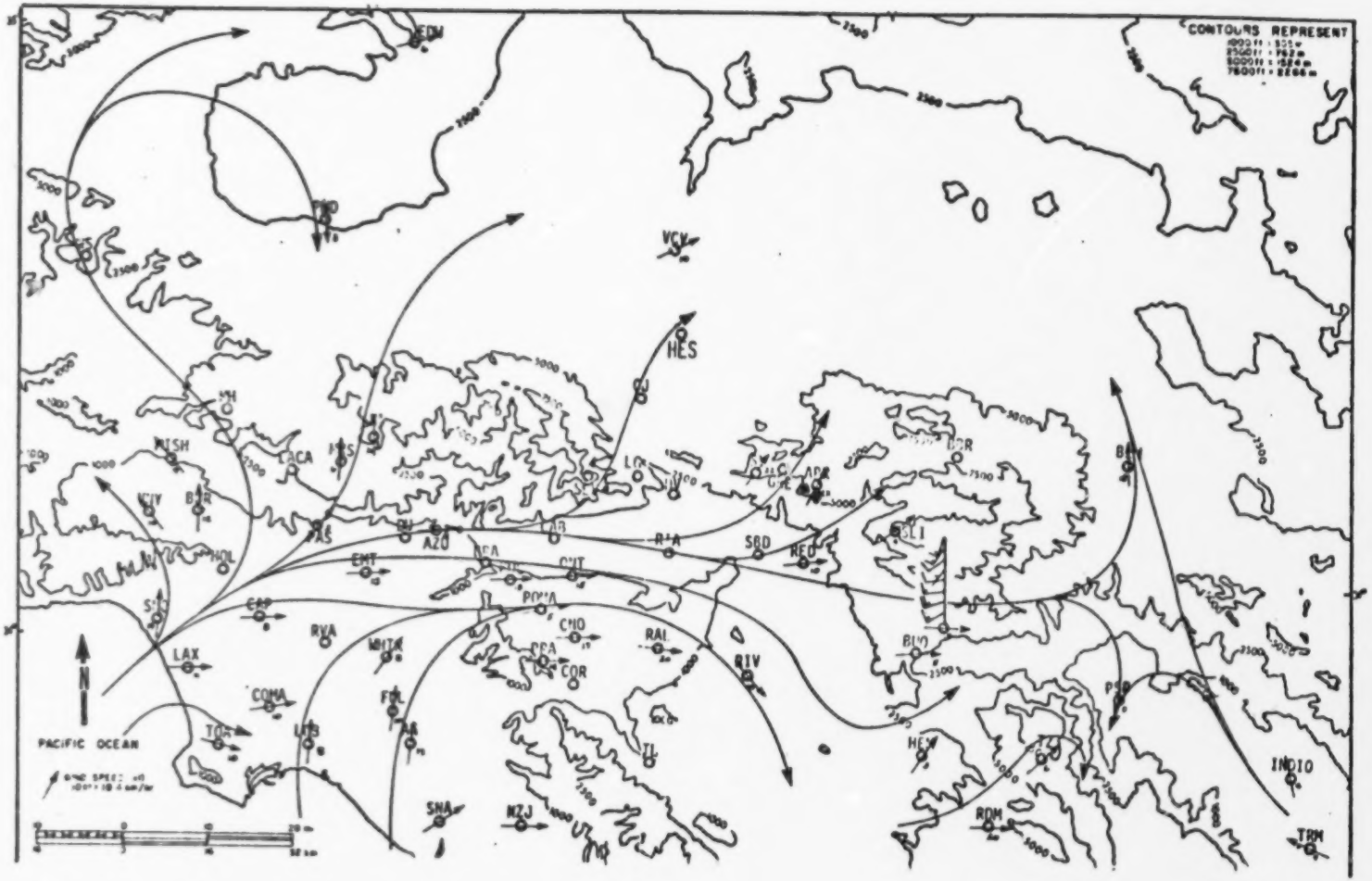


Fig. III-14. VERTICAL PROFILE OVER HESPERIA (HES) AUGUST 24, 1973, 1546 PDT



♦ Skyforest
▲ Strawberry Mt. Lookout

Fig. III-15. STREAMLINES FOR 1600 PDT, 8/24/73

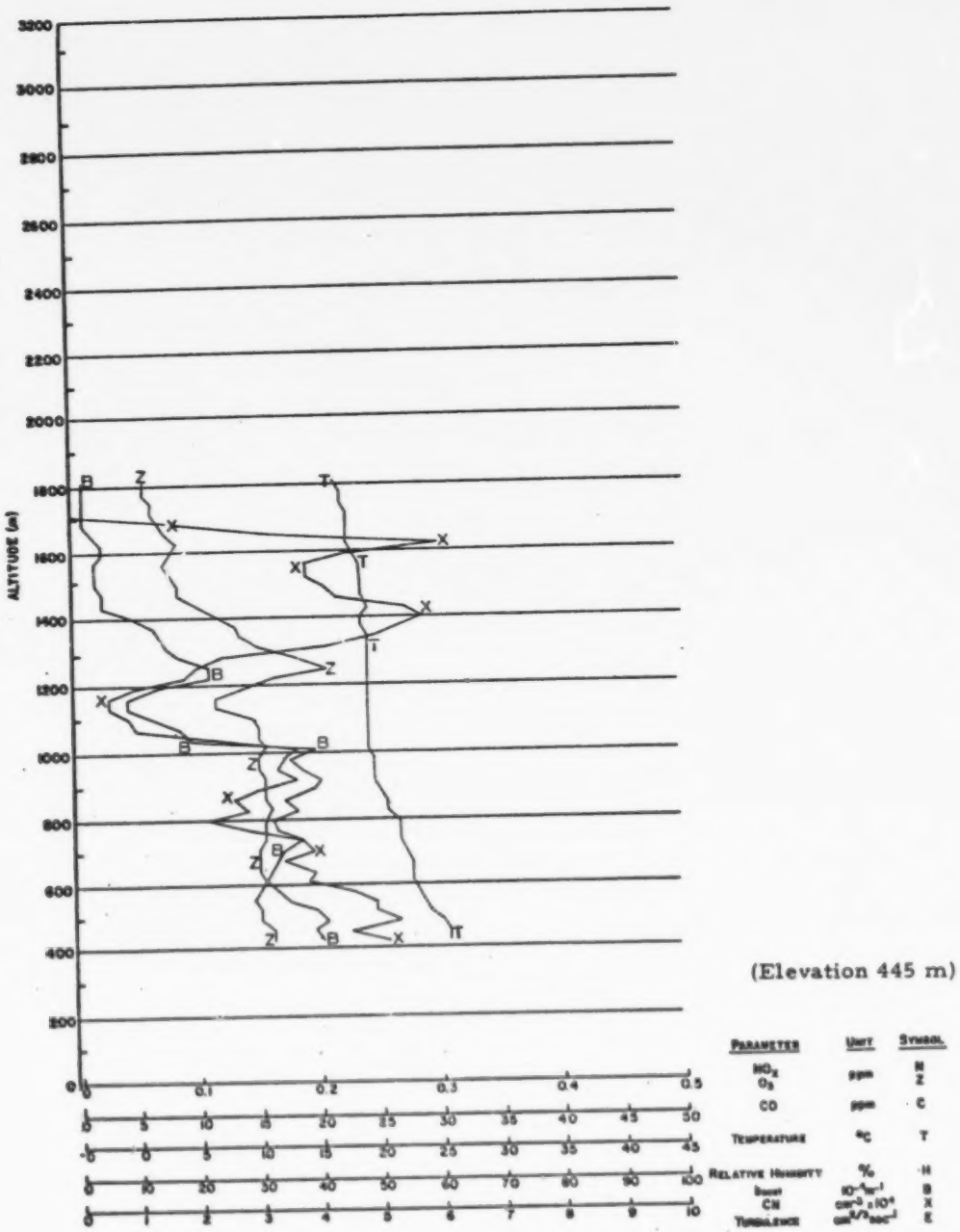


Fig. III-16. VERTICAL PROFILE OVER CABLE (CAB)
AUGUST 24, 1973, 1200 PDT

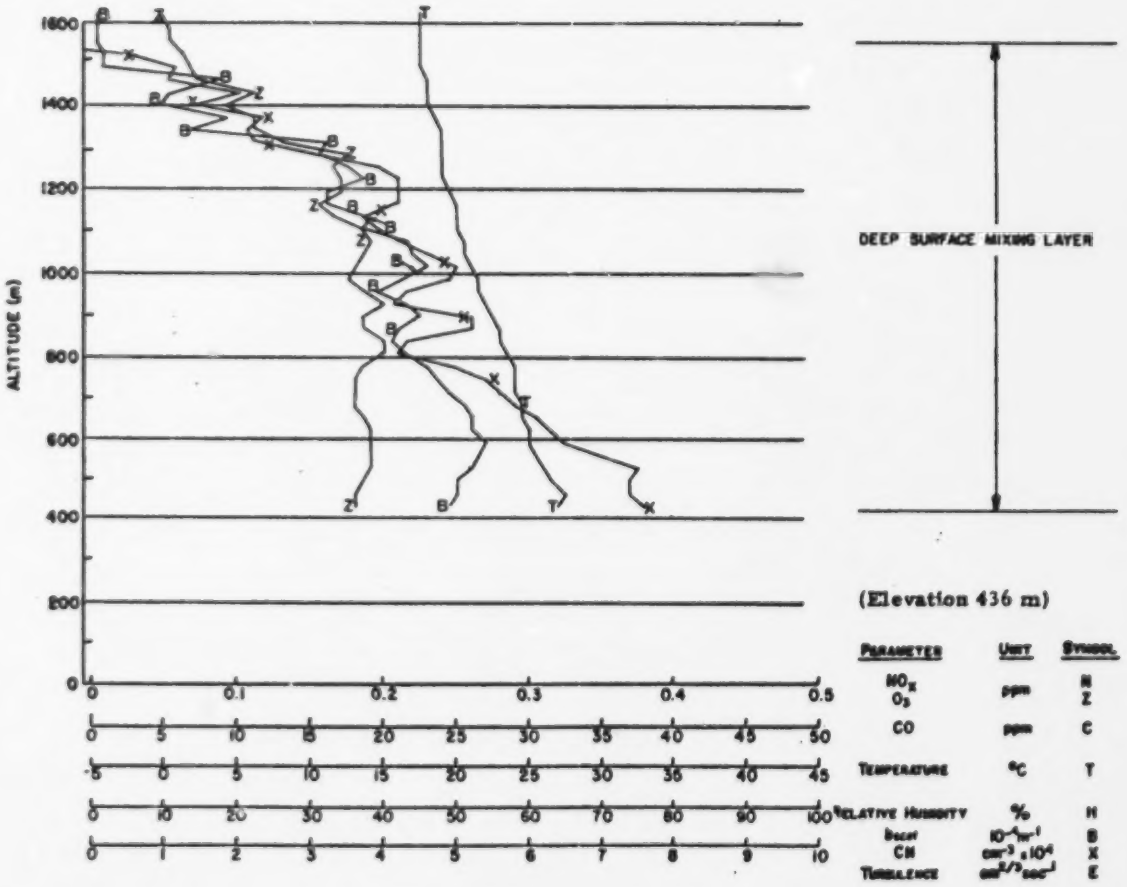


Fig. III-17. VERTICAL PROFILE OVER RIALTO (RIA)
AUGUST 24, 1973, 1321 PDT

in the western Los Angeles basin during the stagnant period prior to onset of the flow pattern shown in Fig. II-15.

Data from both August 16 and 24 suggest strongly that ozone or precursors originating in the metropolitan area moved eastward through the Los Angeles Basin, through Cajon Pass, and up the mountain slopes. Evidence is shown of the arrival of these air parcels at Arrowhead and Hesperia (about 90-100 km downwind of the central Los Angeles area).

IV. OZONE ALOFT - MECHANISMS AND PERSISTENCE

Previous chapters have shown the feasibility of the export of large quantities of ozone from urban areas and the transport, in a single day, of ozone to rural areas. This chapter shows that, in the absence of scavenging substances, ozone is stable for long periods of time and that multiday transport is possible. One method of isolating ozone from fresh emissions or other scavengers is to confine it to a layer aloft. There has recently been much discussion of the source of ozone in layers aloft, and this chapter also presents several examples of normal meteorological mechanisms for transporting ozone and other pollutants from the surface to elevated layers.

A. Mechanisms for Trapping Pollutants in Layers Aloft

Numerous mechanisms exist for creating well-defined layers aloft that contain air which was previously in contact with the surface. The examples presented here are divided into two categories: (1) creation of layers by undercutting of air that was previously within the surface mixing layer and (2) creation of layers by buoyant lifting or transport of air from the surface.

Examples of undercutting include the isolation of air aloft by the formation of a radiation inversion below and the undercutting or lifting of one air mass by another. Figure IV-1 is a repeat of a vertical profile over El Monte, California on July 25, 1973 (previously Fig. II-8). In this figure, the sea breeze extends from the surface to about 450 m and has undercut the air mass above. The air between 450 m and about 700 m msl was previously part of the surface mixing layer, but was isolated from the surface by the onset of the cooler marine air below. On a much larger scale, frontal systems act much like the sea breeze in Fig. IV-1 with one air mass lifting or undercutting another. The sea breeze in effect is a miniature cold front.

Figure IV-2 is an early morning vertical profile over Brackett Airport on July 26, 1973, one day after the profile in Fig. IV-1. Several distinct layers are seen in this figure. The layers between 450 m msl and the top of the graph exist in a very stable atmosphere. These layers have been isolated from the surface (and from surface emissions) by the nocturnal radiation inversion, and the ozone aloft has probably remained from the previous day. The ozone below 450 m msl, however, has been depleted by fresh emissions into the surface layer.

The layer roughly between 520 and 730 m msl is an example of a pollutant layer aloft created by buoyant lifting from the surface. The situation in this case is quite complicated. This layer was just

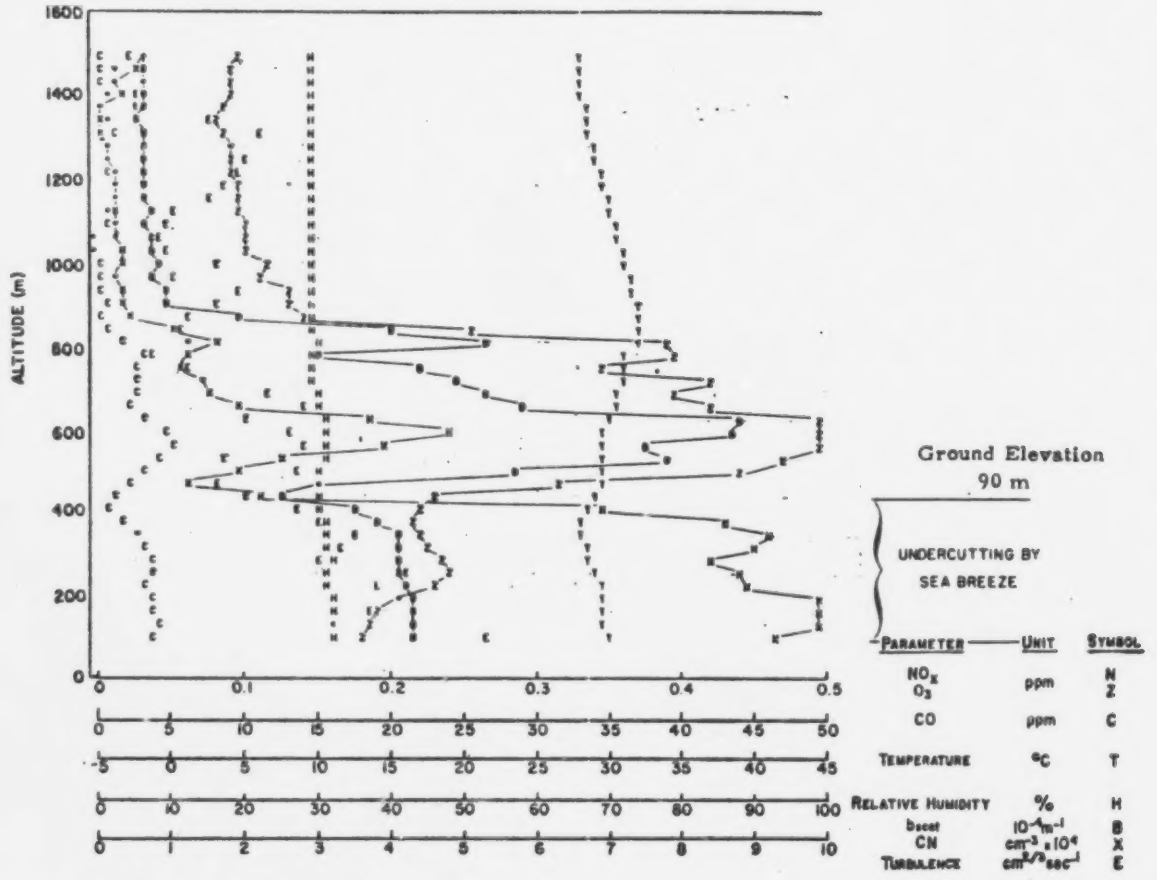


Fig. IV-1. VERTICAL PROFILE AT EL MONTE (EMT) JULY 25, 1973, 1656 PDT, SHOWING UNDERCUTTING BY THE SEA BREEZE

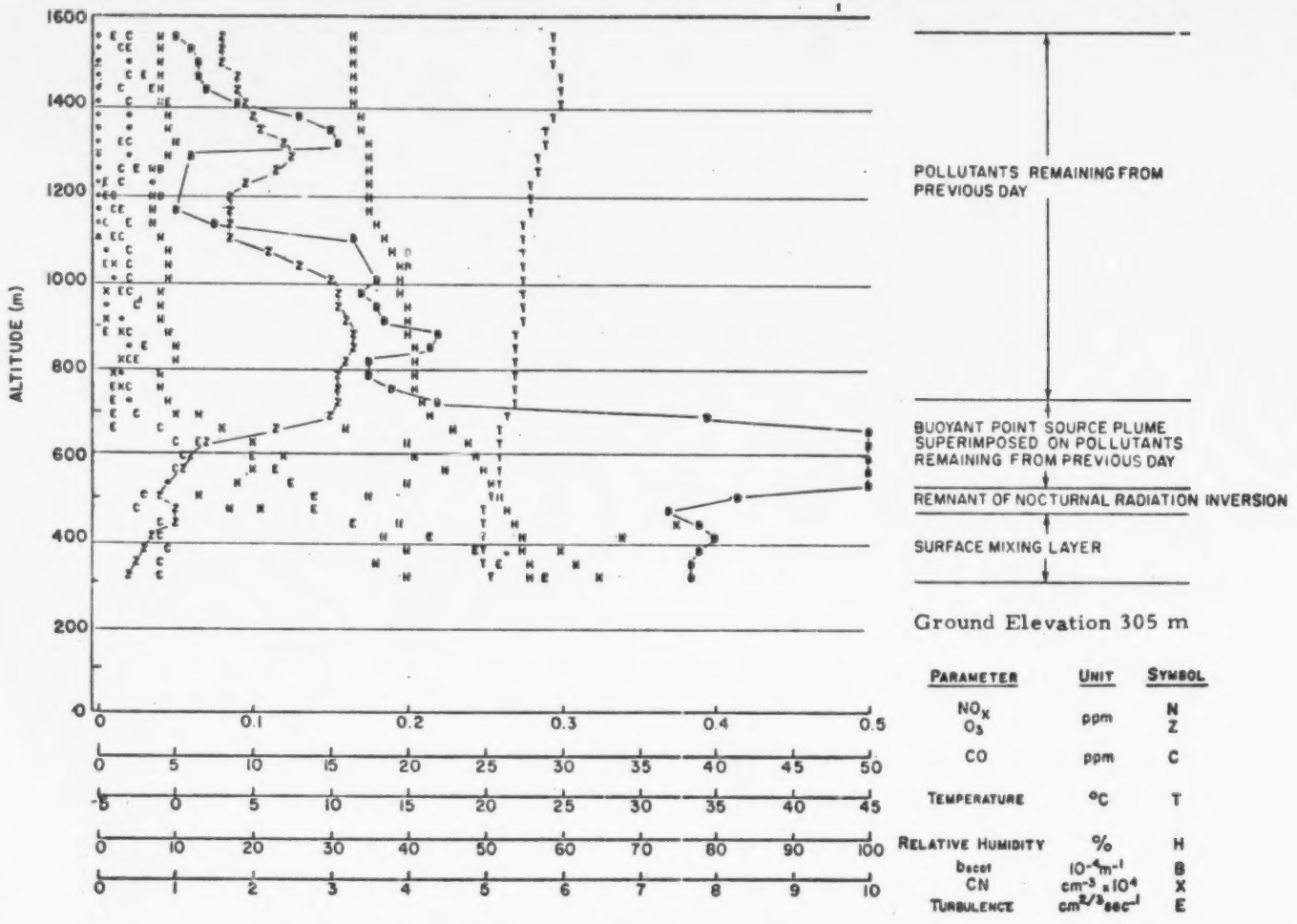


Fig. IV-2. VERTICAL PROFILE OVER BRACKETT (BRA) JULY 26, 1973, 0825 PDT, SHOWING BUOYANT PLUME AND UNDERCUTTING BY RADIATION INVERSION

described as being isolated from the surface. Actually, the high b_{scat} and other pollutant readings are due to a point source plume with enough buoyancy to penetrate the radiation inversion. Since the atmosphere is stable, the plume has reached an equilibrium height where it is no longer buoyant and has stabilized to form a layer. The buoyant plume was able to penetrate the inversion, but other emissions at ground level were prevented by the inversion from mixing higher than about 450 m msl. Note that the ozone was also somewhat depleted by NO_x emissions in the plume. In the presence of strong sunlight however, it is probably possible under some circumstances to produce ozone photochemically in an elevated point source plume.

Other examples of buoyancy mechanisms which can generate layers aloft are: urban heat islands which cause urban air to be warmer (more buoyant) than surrounding air and can generate elevated urban plumes under certain conditions, convective cells which occur over heated terrain and lift air from the surface, and heated mountain slopes which can cause localized heating and upslope flow. Figure IV-3 is a profile at Rialto, California, near the San Gabriel Mountains. Two layers are evident in the figure separated by a layer of relatively clear air. The surface mixing layer is capped by a slight inversion topping at about 1050 m msl; however, air near the mountains is heated by contact with the slopes and flows upslope to an altitude at which it is at equilibrium, forming a second layer.

B. Overnight Persistence of Ozone

The ability of ozone to survive in the absence of sunlight can be demonstrated by observation of the vertical distribution of O_3 at various times through the night in a layer separated from surface sources by a stable layer. The data for such a demonstration has been provided by a 24-hour study of pollutants over the San Bernardino-Riverside air basin east of Los Angeles on July 26 and 27, 1973. As part of an observational program, aircraft soundings were made over six locations at about 1700 and 2300 PDT on July 26 and about 0200 and 0500 PDT on July 27.

The names and three letter identifiers of the six sampling locations are listed in Table IV-1. Their locations can be found in any of the several foregoing figures showing maps of Los Angeles and vicinity. The results of the overnight observation of O_3 are also summarized in Table IV-1. Ozone data were studied for an elevated layer free of surface influences. The layer between 1000 and 1500 m (3000 to 4500 ft) msl was selected so that all soundings would be continuous to the top of the layer, and the bottom of the layer would be above the surface inversion on all 24 soundings. Averages of observed

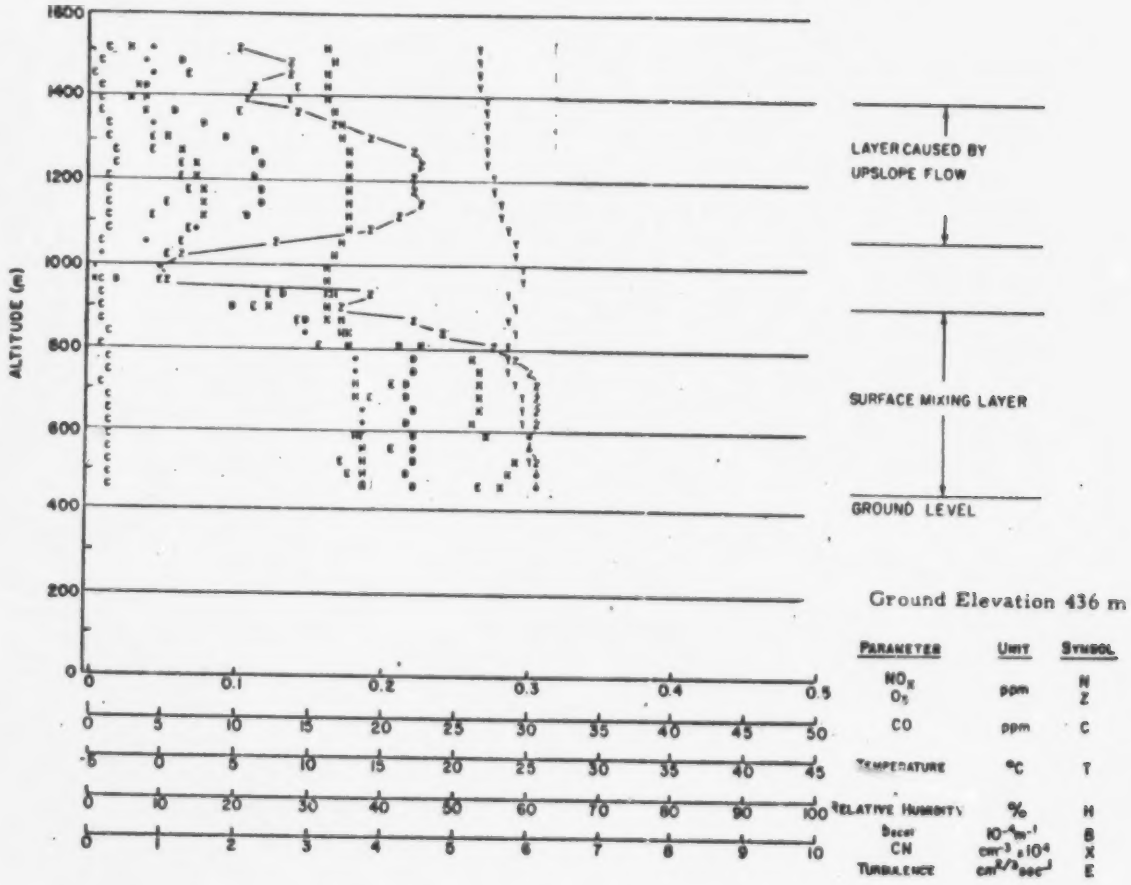


Fig. IV-3. VERTICAL PROFILE AT RIALTO (RIA) JULY 19, 1973, 1738 PDT, SHOWING LAYER CAUSED BY UPSLOPE FLOW

Table IV-1

Overnight Ozone Concentrations

Location	Times PDT			
	July 26 17 PDT	July 26 23 PDT	July 27 2 PDT	July 27 5 PDT
Ontario (ONT)	9.3 13.8 (-2.5)	11.3 0.6 (3.5)	13.1 1.2 (3.5)	12.0 0.2 (7.5)
Rialto (RIA)	16.4 20.4 (-3.5)	10.7 0.2 (2.5)	12.5 0.4 (2.5)	13.6 0.2 (5)
Redlands (RED)	16.8 16.6 (-4)	13.4 4.8 (1.5)	11.5 3.7 (3.5)	12.1 6.3 (3.5)
Riverside (RAL)	9.8 15.4 (-3.5)	11.0 2.4 (2)	10.6 0.2 (4.5)	11.4 0.1 (6)
Corona (COR)	10.4 12.3 (-2.5)	11.0 0.1 (5)	11.1 0.3 (5)	11.7 0.3 (6)
Bracket (BRA)	9.7 20.7 (-4)	11.9 0.2 (4.5)	13.1 7.2 (2)	14.6 0.1 (6.5)
Average	12.1 16.5 (-3.5)	11.6 1.4 (3)	12.0 2.2 (3.5)	12.6 1.2 (5.5)

The upper left hand number in each set is the average O_3 concentration (pphm) between 1000 m and 1500 m. The lower left hand number is the average O_3 concentration (pphm) in the first 200 m above ground. The number in parentheses is the temperature °C at 1000 m minus the average temperature in the first 200 m above ground.

ozone were calculated for both this layer and for first the 200 m above the surface for all soundings. The upper number in each group of three in Table IV-1 is the mean O_3 concentration for the elevated layer while the lower number is for the surface 200 m thick layer. The number in paretheses in each group is an indicator of stability of the layer below about 1000 m (3000 ft) msl. The number is the difference in temperature in degrees centigrade between the 1000 m msl temperature and the average temperature in the first 200 m above the ground.

There are many reactions known which can consume O_3 in the lower atmosphere. By far the fastest of these is the following:

$$NO + O_3 \longrightarrow NO_2 + O_2.$$

The rate constant for this reaction is about 0.3 $pphm^{-1}\ min^{-1}$ (Johnston and Crosby, 1954), which means that, at a constant NO concentration of 1 pphm, the half-life of O_3 for this reaction is less than 3 minutes. In the absence of the solar radiation necessary to produce O_3, NO from the fresh exhaust of combustion sources therefore quickly scavenges O_3 . This is seen in Table IV-1 where O_3 concentrations near the ground fall below the 4 pphm background value during the night due to the continuous introduction of fresh emissions into the surface layer.

As the temperature differentials in Table IV-1 indicate, air above about 1000 m is isolated from the surface layer throughout the night by a strong ground based temperature inversion that is established at all locations between 1700 and 2300 PST. Cut off from sources of NO, O_3 at the upper levels appears to be quite stable, as shown by concentrations of 12-13 pphm - well above background - that persist through the night. In all 24 soundings studied, O_3 and b_{scat} were well correlated between 1000 and 1500 m, and condensation nuclei (CN) counts at these levels were low. These conditions are typical of well-aged polluted air.

Examples of the soundings from one location, Riverside, are given in Fig. IV-4 to IV-7. The high ozone levels existing throughout the night above the surface mixing layer are evident in these figures. From these figures and Table IV-1 one can see that the ozone aloft is quite stable and that the concentrations do not decrease significantly throughout the night, indicating a half-life for ozone in the atmosphere of something greater than 12 hours.

Thus, the data show that ozone, once formed and in the absence of other pollutants to scavenge it, is stable in the atmosphere at high concentrations for many hours, even in the absence of sunlight.

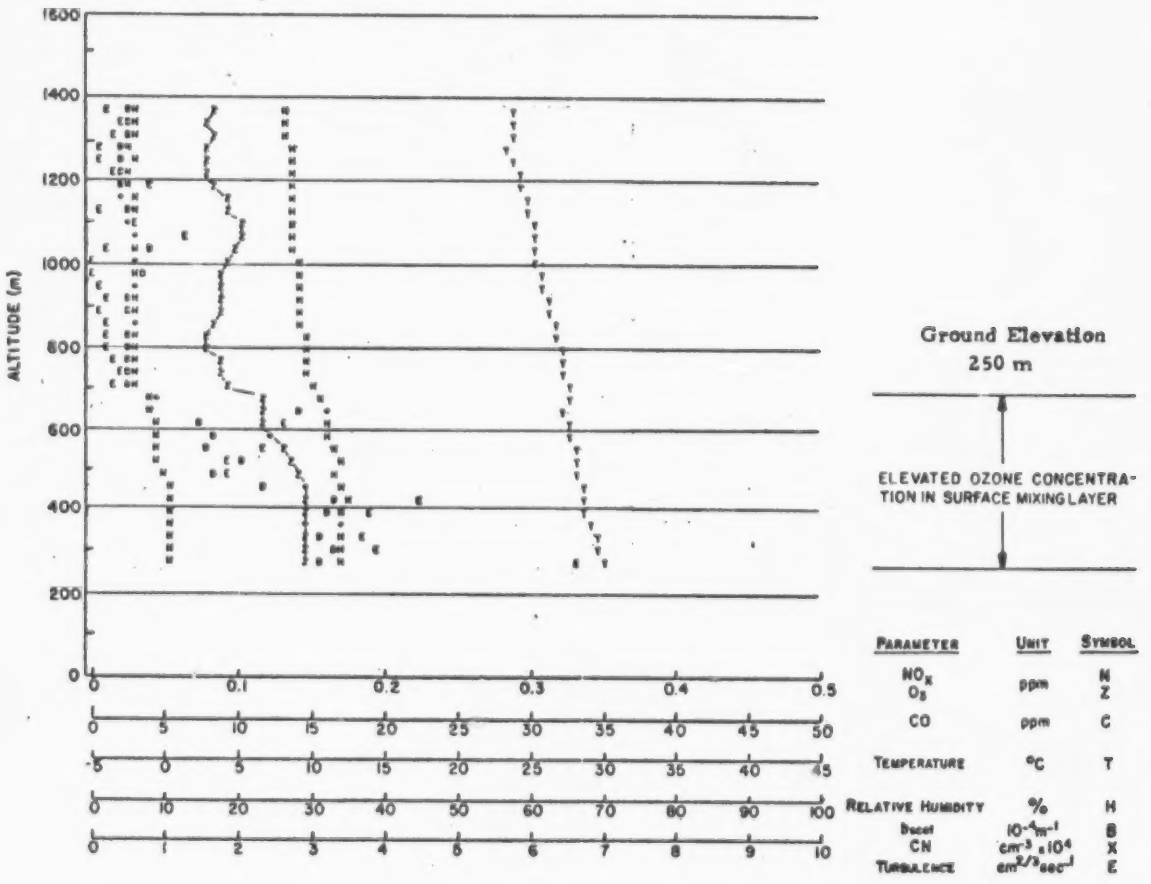


Fig. IV-4. VERTICAL PROFILE OVER RIVERSIDE (RAL)
JULY 26, 1973, 1638 PDT

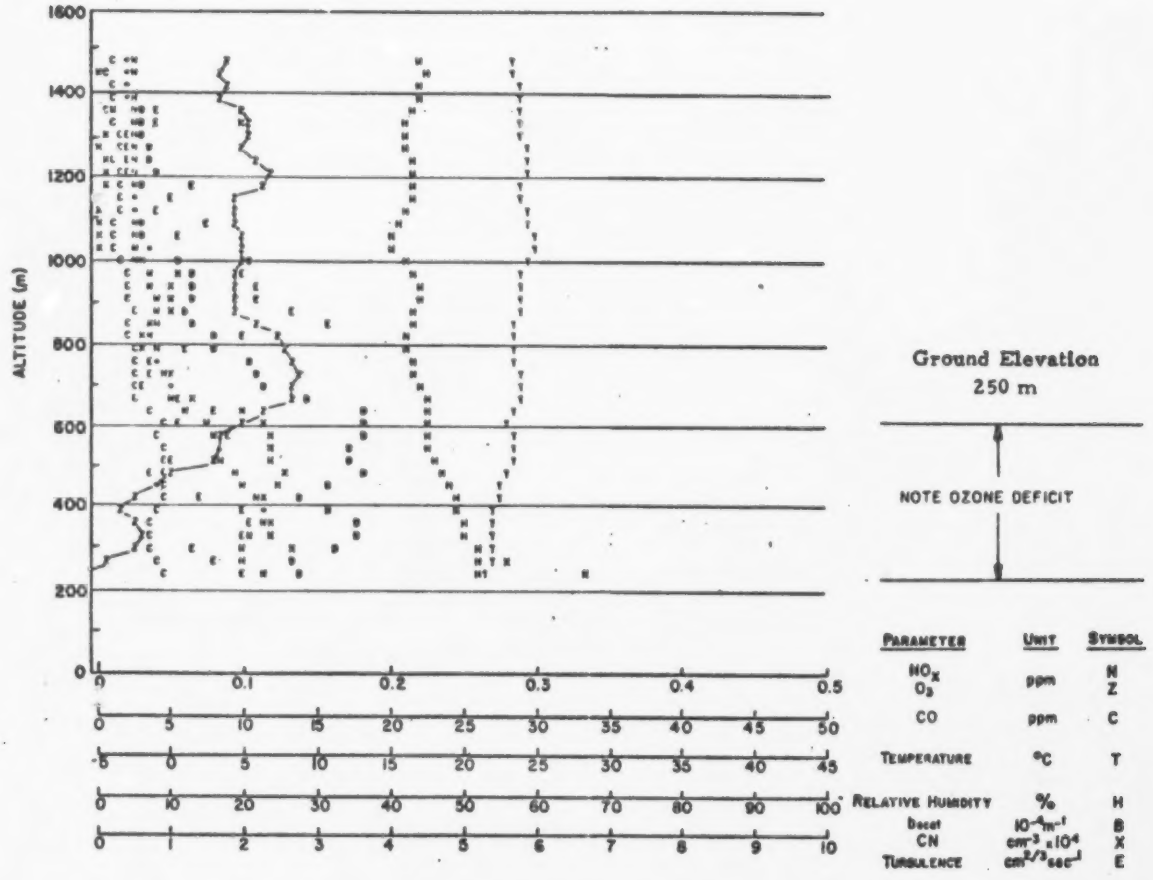


Fig. IV-5. VERTICAL PROFILE OVER RIVERSIDE (RAL)
JULY 26, 1973, 2239 PDT

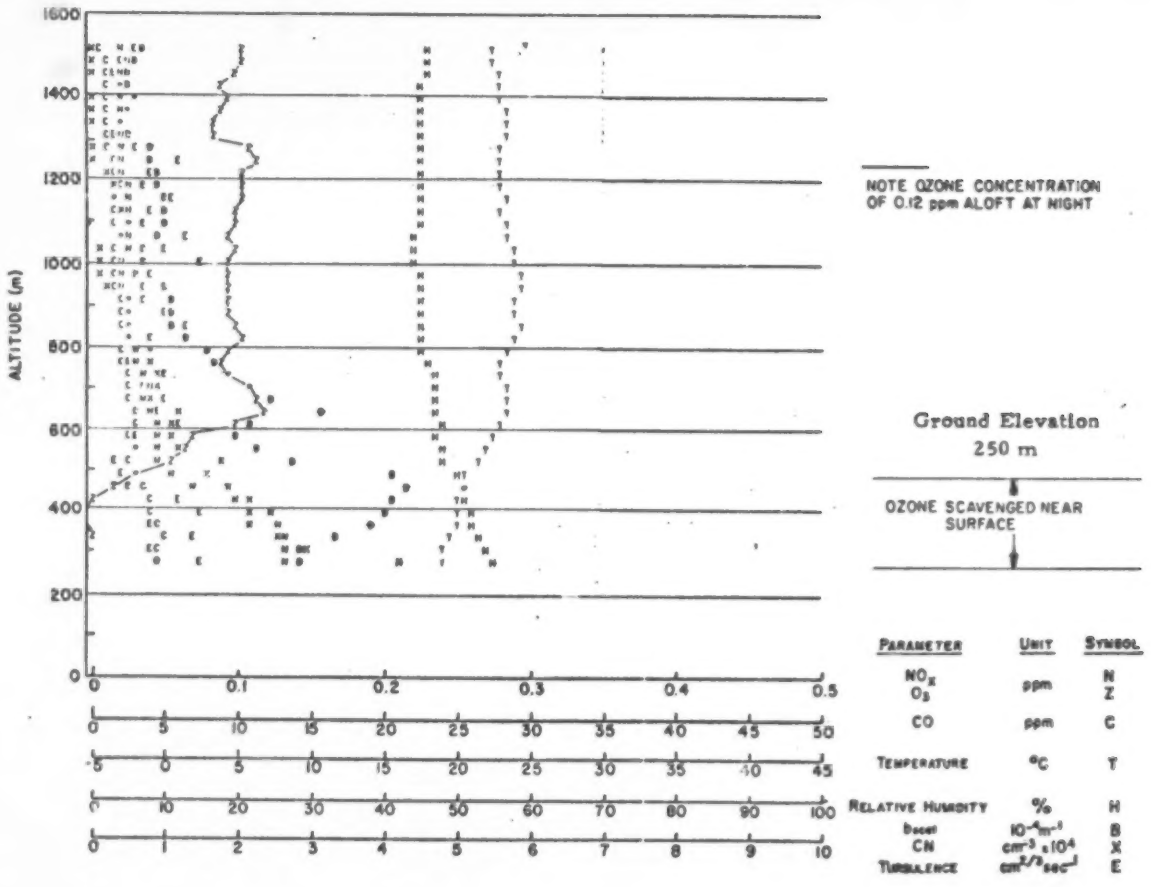

ALTITUDE (m)
1600
1400
1200
1000
800
600
400
200
0
0 0.1 0.2 0.3 0.4 0.5
0 5 10 15 20 25 30 35 40 45 50
-5 0 5 10 15 20 25 30 35 40 45
0 10 20 30 40 50 60 70 80 90 100
0 1 2 3 4 5 6 7 8 9 10
NOTE OZONE CONCENTRATION OF 0.12 ppm ALOFT AT NIGHT
Ground Elevation 250 m
OZONE SCAVENGED NEAR SURFACE
PARAMETER UNIT SYMBOL
NO_x ppm N
O_3 ppm Z
CO ppm C
TEMPERATURE °C T
RELATIVE HUMIDITY % H
bscat $10^{-4}m^{-1}$ B
CN $cm^{-3} \times 10^4$ X
TURBULENCE $cm^{2/3}sec^{-1}$ E

Fig. IV-6. VERTICAL PROFILE OVER RIVERSIDE (RAL)
JULY 27, 1973, 0122 PDT

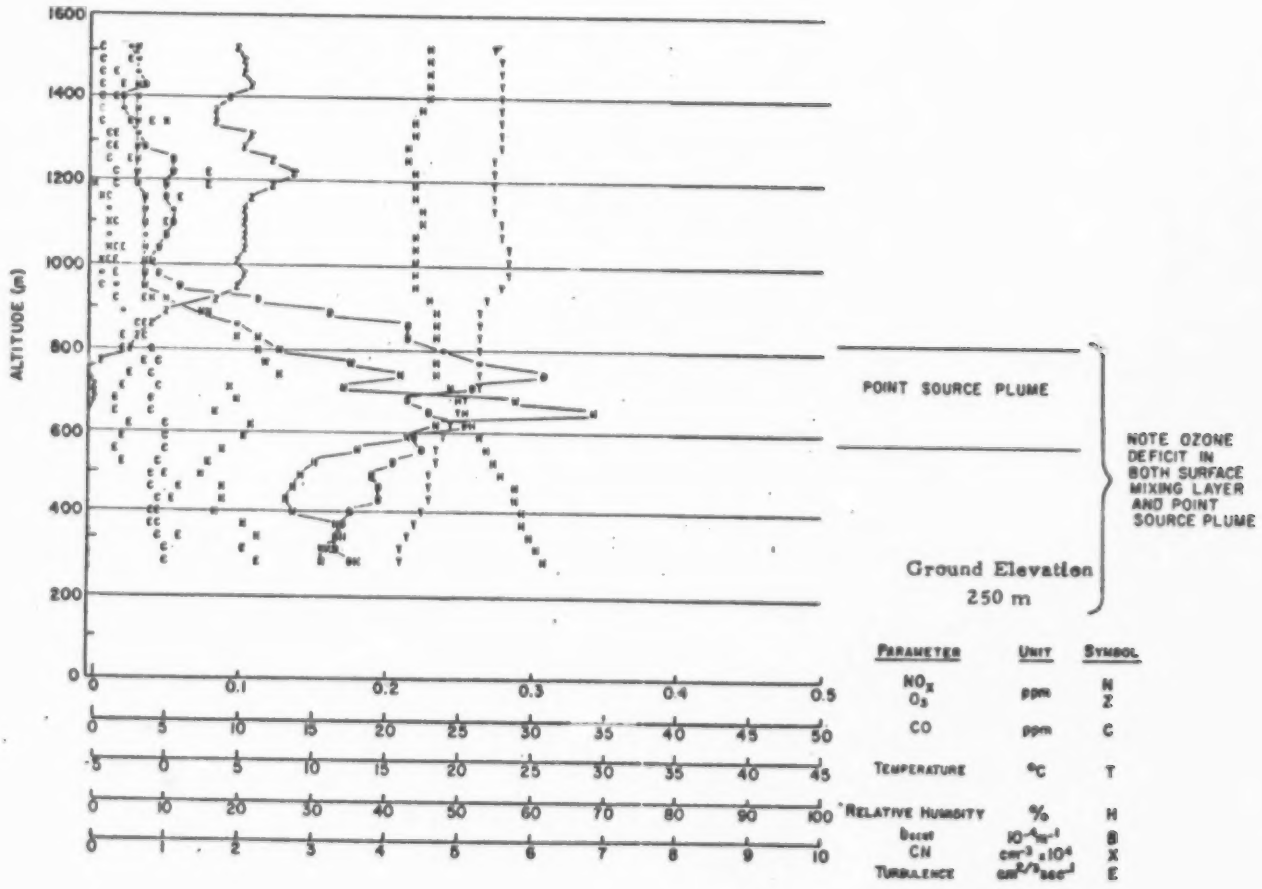


Fig. IV-7. VERTICAL PROFILE OVER RIVERSIDE (RAL)
JULY 27, 1973, 0500 PDT

C. Ozone Persistence in Rain

Figures IV-8 and IV-9 show profiles made over Shepherd Airport (SHE) in the Los Angeles area. These traverses were made on a fairly clear, rainy day during which photochemical processes should have been minimal. In the absence of photochemistry, the ozone is destroyed by the primary pollutants and the depth to which the polluted air has mixed during the day is indicated by the depth of the ozone deficit. The morning sounding indicates a mixing depth of about 300 m msl while, by afternoon, the fresh pollutants had mixed up to 1000 m. Note that in Fig. IV-8 in the quite clean air at 1600 m, the ozone level is between 0.03 and 0.04 ppm (approximately background level) even in the rain.

Even though ozone is quite reactive, the above data show that, in the absence of other reactants, it is stable and will remain in the atmosphere a long time. This would be in agreement with Junge (1963) who has mentioned that the residence time of ozone in the troposphere should be on the order of one to two months.

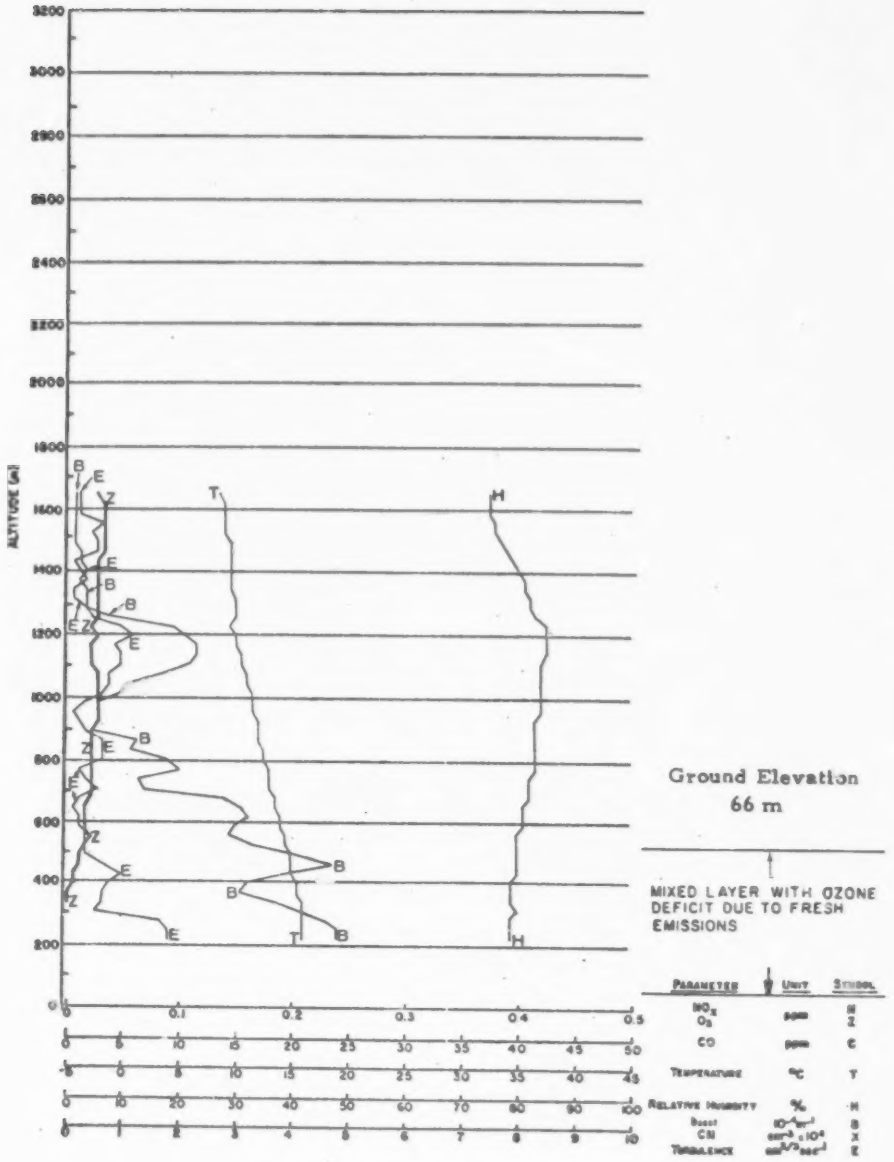


Fig. IV-8. VERTICAL PROFILE OVER SHEPHERD (SHE) IN THE RAIN, OCTOBER 18, 1972, 1020 PDT

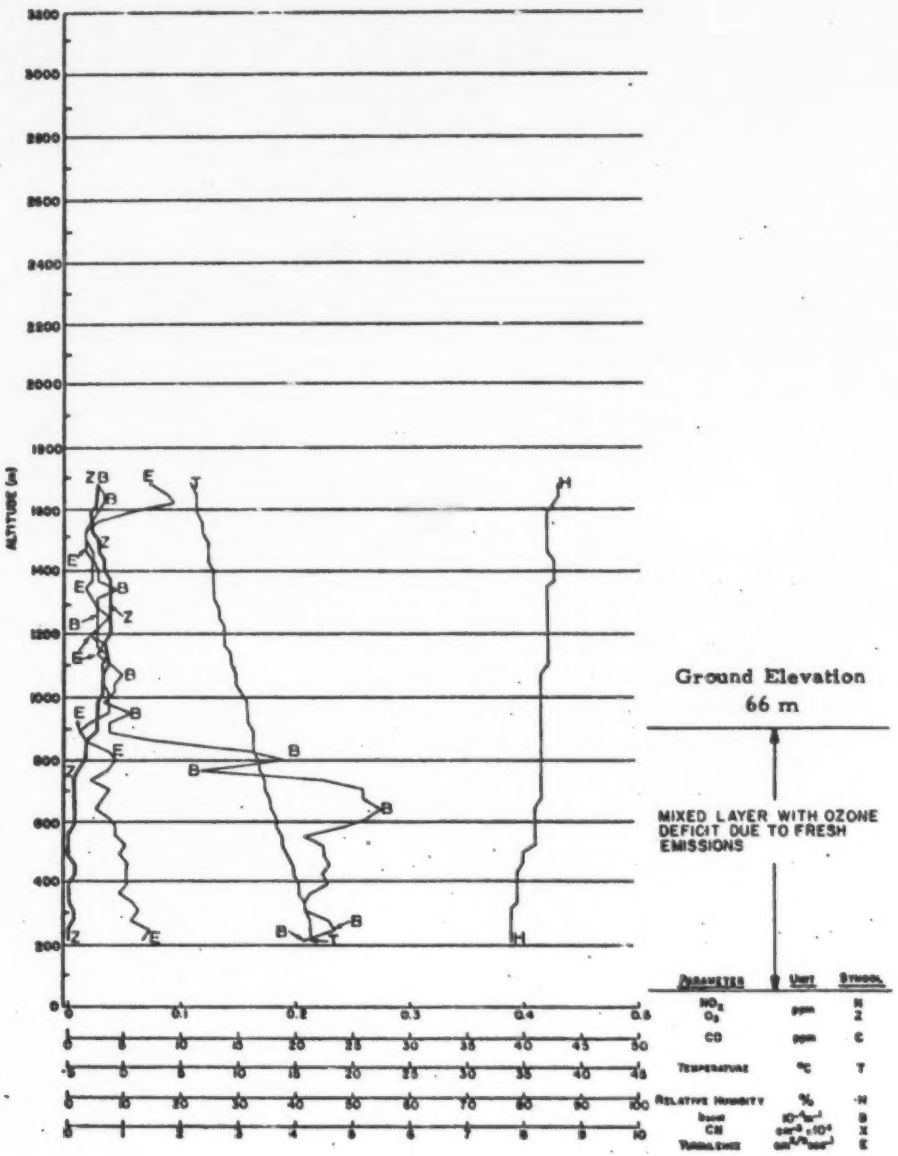


Fig. IV-9. VERTICAL PROFILE OVER SHEPHERD (SHE) IN THE RAIN, OCTOBER 18, 1972, 1357 PDT

V. ESTIMATES OF POTENTIAL DOWNWIND EFFECTS

The Los Angeles Air Basin is a natural area in which to study the formation and meso-scale transport of ozone, because of the frequency of occurrence of high ozone concentrations and their extensive documentation. The complicated topography surrounding the basin makes it less than ideal, however, for the study of long-range transport. For this purpose it is instructive to employ standard diffusion estimates to calculate the effects that an ozone source the size of the Los Angeles urban region could have downwind in flat terrain. This chapter presents the results of such an exercise.

The calculations were based on a number of simplifying but conservative assumptions. These are listed below.

1. Ozone concentrations can be maintained for extended periods in the absence of scavengers such as NO. On the basis of elevated layer observations in the Los Angeles area, a lifetime of at least 12 hours is indicated.

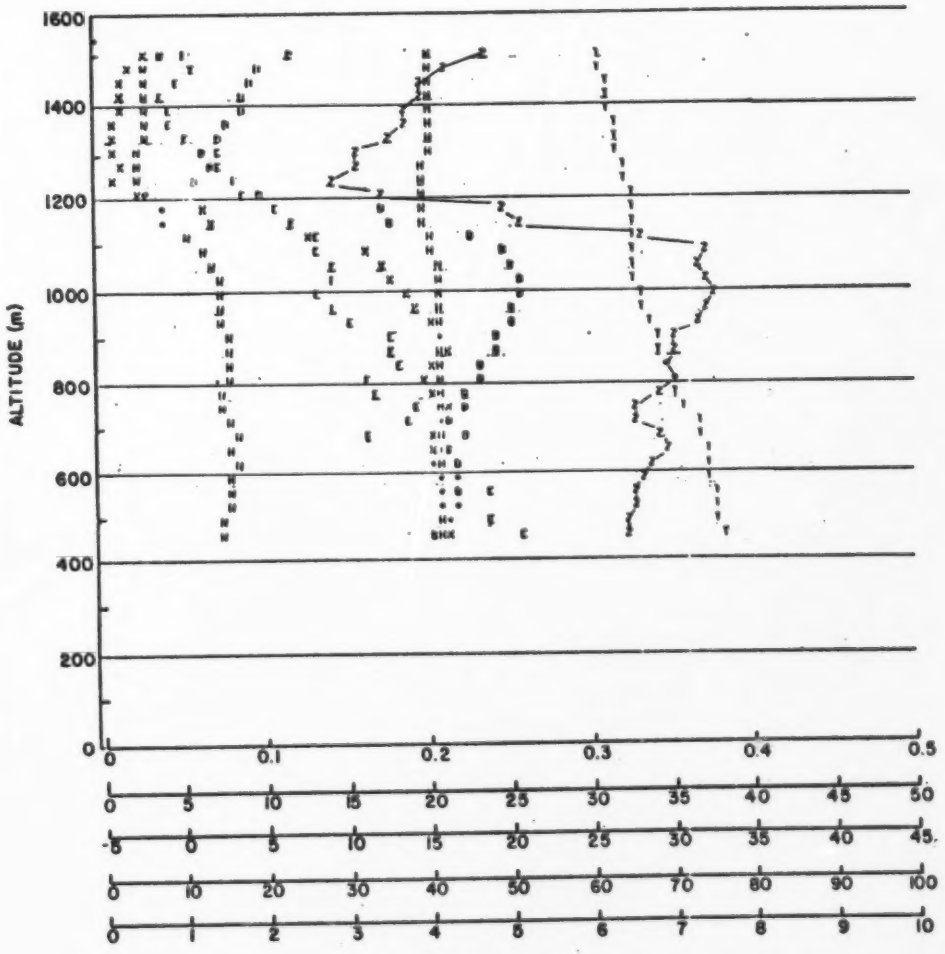
2. The polluted layer increases in depth by a factor of two during the 12-hour period. This factor was put in to be conservative. Typical mixing layers tend to be less than 1200 m deep.

3. The urban plume continues to diffuse according to standard diffusion laws with no effects of terrain.

4. No new emissions are injected into the urban plume, and no new ozone is produced by photochemical reaction.

The urban plume was assumed gaussian, and August 16, 1973 was selected as a representative day for the purpose of establishing the plume parameters. Figure V-1 shows the afternoon aircraft sounding for Redlands on this day, taken at 1700 PDT. An average ozone level of about 0.35 ppm is indicated for the layer from the surface to a height of 640 m (2100 ft) above ground. Surface oxidant values indicate that the crosswind width of the Los Angeles Metropolitan Area urban plume extended at least from San Bernardino past Riverside (approximately 24 km or 15 miles). Accordingly, a peak ozone concentration of 0.35 ppm (0.31 ppm above background levels) and a width of 24 km (σ = 5.6 km) were taken as the initial conditions of the plume.

For the purposes of estimating downwind concentrations, it is appropriate to assume a C stability category (Turner, 1969). The wind speed was assumed constant at 5 m/s. Under these conditions, a σ_y



Ground Elevation 480 m

PARAMETER	UNIT	SYMBOL
NO_x	ppm	N
O_3		Z
CO	ppm	C
TEMPERATURE	°C	T
RELATIVE HUMIDITY	%	H
b_{scat}	$10^{-4}m^{-1}$	B
CN	$cm^{-3} \times 10^4$	X
TURBULENCE	$cm^{2/3}sec^{-1}$	E

Fig. V-1. VERTICAL PROFILE AT REDLANDS (RED)
AUGUST 16, 1973, 1700 PDT

(crosswind) value of 5.6 km would occur at a distance of 95 km downwind of an effective point source. At a distance of 200 km from Redlands (295 km from the hypothetical source), the σ_y value would have increased to 17 km. Using assumption 2 above and the expected increase in plume width:

$$\text{Conc. at 200 km from Redlands} = \frac{5.6}{17x2} \text{ (Conc. at Redlands).}$$

If a background concentration of 0.04 ppm is assumed, the above equation becomes:

$$\text{Conc. at 200 km from Redlands} = \frac{5.6}{17x2} \times 0.31$$

or

$$\text{Conc. at 200 km from Redlands} = 0.05 \text{ ppm.}$$

These calculations indicate that the initial ozone conditions in an area such as Redlands could provide a contribution of about 0.05 ppm above background at a downwind distance of about 200 km (about 12 hours travel time). This contribution, together with the assumed background of 0.04 ppm, would exceed the ozone ambient standard. Adding in the fact that Redlands is already over 60 km from the effective pollutant source, a source area such as Los Angeles could possibly cause ozone standards to be exceeded as far as 260 km or more away.

The above calculations are believed to be a conservative example of potential downwind effects under those conditions when it is assumed that no ozone-destroying mechanisms exist.

VI. CONCLUSIONS

1. Analyses of observational data on two days in the Los Angeles Basin indicate that ozone and/or its precursors were transported from the metropolitan area approximately 100 km downwind to the eastern portion of the Basin. The data indicate that most of the ozone and other pollutant burdens (above background level) at the downwind locations in the afternoon were due to precursors emitted earlier in the day or even during the previous night in the western basin upwind. The meteorology of the basin is such that pollutants which accumulate during the night and morning hours over the western basin are transported eastward in a daily pulsing fashion. The contribution to the ozone burden in the eastern basin due to the western basin appears to be sufficient to cause the ambient air standard (0.08 ppm) to be exceeded even in the absence of any local contributions.

2. Observations of ozone in layers aloft both at night and in the rain indicate that ozone is stable in the absence of other substances to scavenge it. Ozone has been observed to remain undiminished at high concentrations in layers aloft out of contact with the ground for periods in excess of 12 hours, indicating a lifetime in the atmosphere of considerably greater than 12 hours.

3. Ozone has been observed in rural areas at concentrations as high as 0.3 ppm with no possible local source. Wind trajectories, vertical profiles of pollutants, and surface pollutant data all indicate the source of the ozone precursors to be urban areas, in some cases as far away as 100 km.

4. Using data from a single (but typical) day in the Los Angeles air basin, extrapolating to flat terrain and using standard diffusion techniques, it has been shown that a source area like the central Los Angeles area could cause ozone concentrations to exceed the Federal standard of 0.08 ppm at locations as far away as 260 km. This estimate is believed to be conservative.

5. From the data presented, it is believed that urban sources can have a substantial effect on ozone concentrations in downwind areas and that this effect can carry over more than one day.

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VIII. ACKNOWLEDGMENTS

The primary data used in this study were obtained in experimental programs performed by MRI and funded by the California Air Resources Board (ARB) and by the Environmental Protection Agency (EPA). The authors would like to thank the ARB for their interest in and cooperation with this EPA-funded study and to compliment both agencies on the degree of interagency cooperation shown throughout the project.

We would also like to thank Metronics Inc. for their cooperation in providing much of the upper air wind data used in the analysis.

Other sources of data were: Loren Crow, consultant; the National Weather Service; the U.S. Forest Service; McDonnell Douglas Aircraft Co.; and the Los Angeles, Orange, San Bernardino, and Riverside County Air Pollution Control Districts.

This report would not have been possible without the many hours of effort put forth by the staff of MRI in collecting and analyzing data and in helping prepare the report. The authors greatly appreciate this effort.

APPENDIX A. DATA FROM JULY 25, 1973 AND SEPTEMBER 21, 1972

TABLE A-1

LIST OF GROUND STATION HOURLY AVERAGE DATA USED IN PREPARING FIG. V-14 FOR 7/25/73

Location	Hour Beginning (PDT)	ppm CO	pphm O_3 (LAAPCD Data Calibration Adjusted)	Depth Of Layer (x 100 ft)	Loadings - Adjusted for Background CO g/m^2	O_3 mg/m^3
LAH	15	6	21	18	3.2	185
RED	17	5	37	17	2.4	339
FON	17	5	45	11	1.5	273
CNO	16	3.5	30	21	1.8	330
CAP	13	6	29	10	1.8	151
POMA	16	7	37	18	3.8	359
LNX (Near LAX)	12	5	1	13	1.8	-
SB	17	4	33	10	1.1	175
AZU	15	3	53	17	1.2	504
PAS	14	7	60	10	2.1	339
CAB	16	3	63	13	0.9	464

TABLE A-2

LIST OF GROUND STATION HOURLY AVERAGE DATA
USED IN PREPARING FIG. II-26 FOR 9/21/72

Location	Hour Beginning (PDT)	ppm CO	pphm O_3 (LAAPCD Data Calibration Adjusted)	Depth Of Layer (x 100 ft)	Loadings - Adjusted for Background CO g/m^2	Loadings - Adjusted for Background O_3 mg/m^2
AN	14	5	18	13	1.8	110
LAH	14	7	20	16	3.4	155
PRA	15	-	23	38	-	437
RUB	16	3	22	40	2.8	436
SB	17	4	14	34	3.6	206
ONT	16	3	6	41	2.9	50
RED	17	2	13	34	1.2	185
FON	16	-	16	39	-	283
CAP	12	6	24	8	1.4	97
LGB	13	6	11	10	1.7	42
POMA	15	6	26	41	7.2	546
LNX	11	7	10	10	2.1	36
WHTR	14	4	26	9	0.9	120

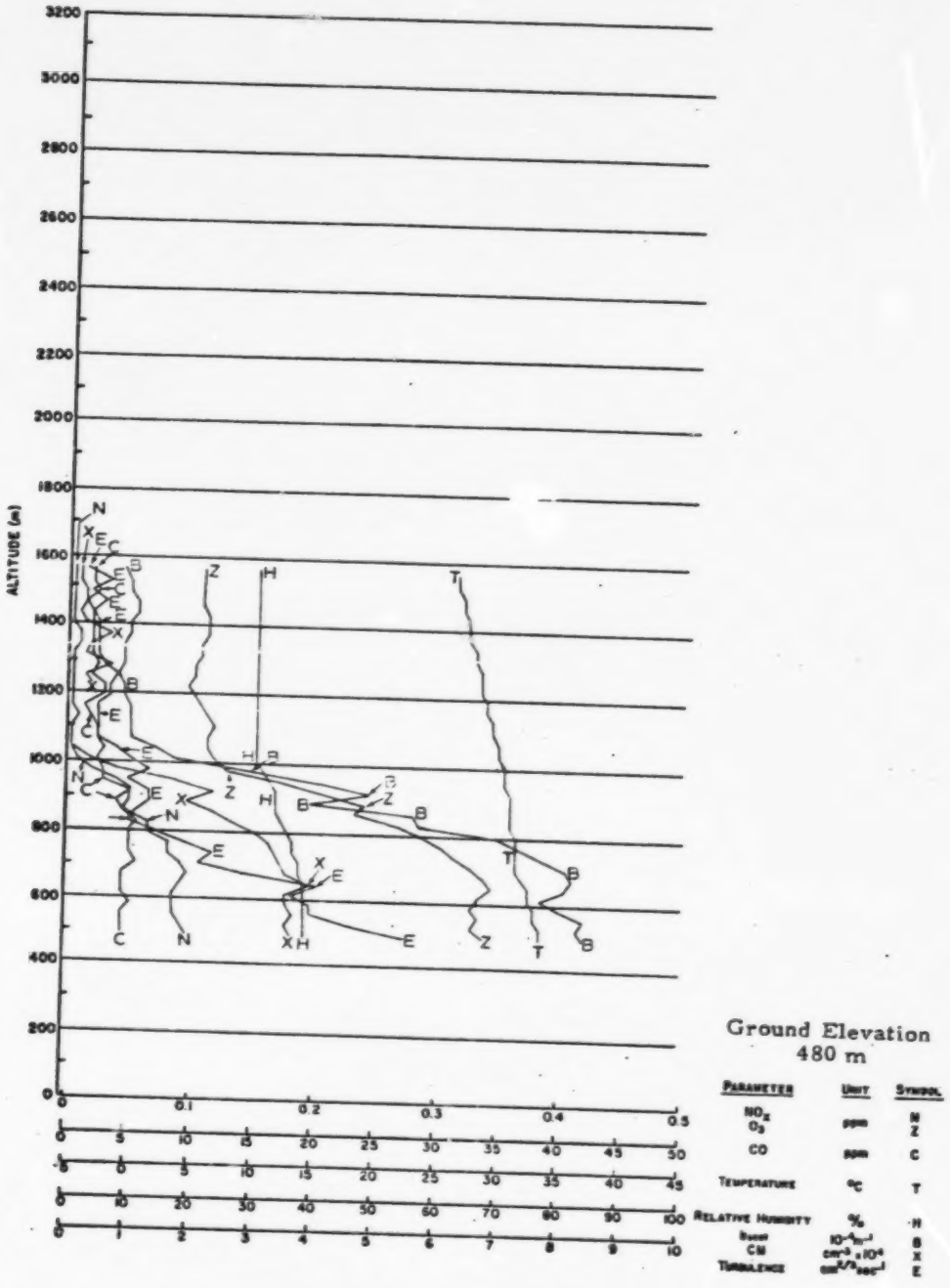

Fig. A-1. VERTICAL SOUNDING OVER REDLANDS (RED)
JULY 25, 1973, 1805 PDT

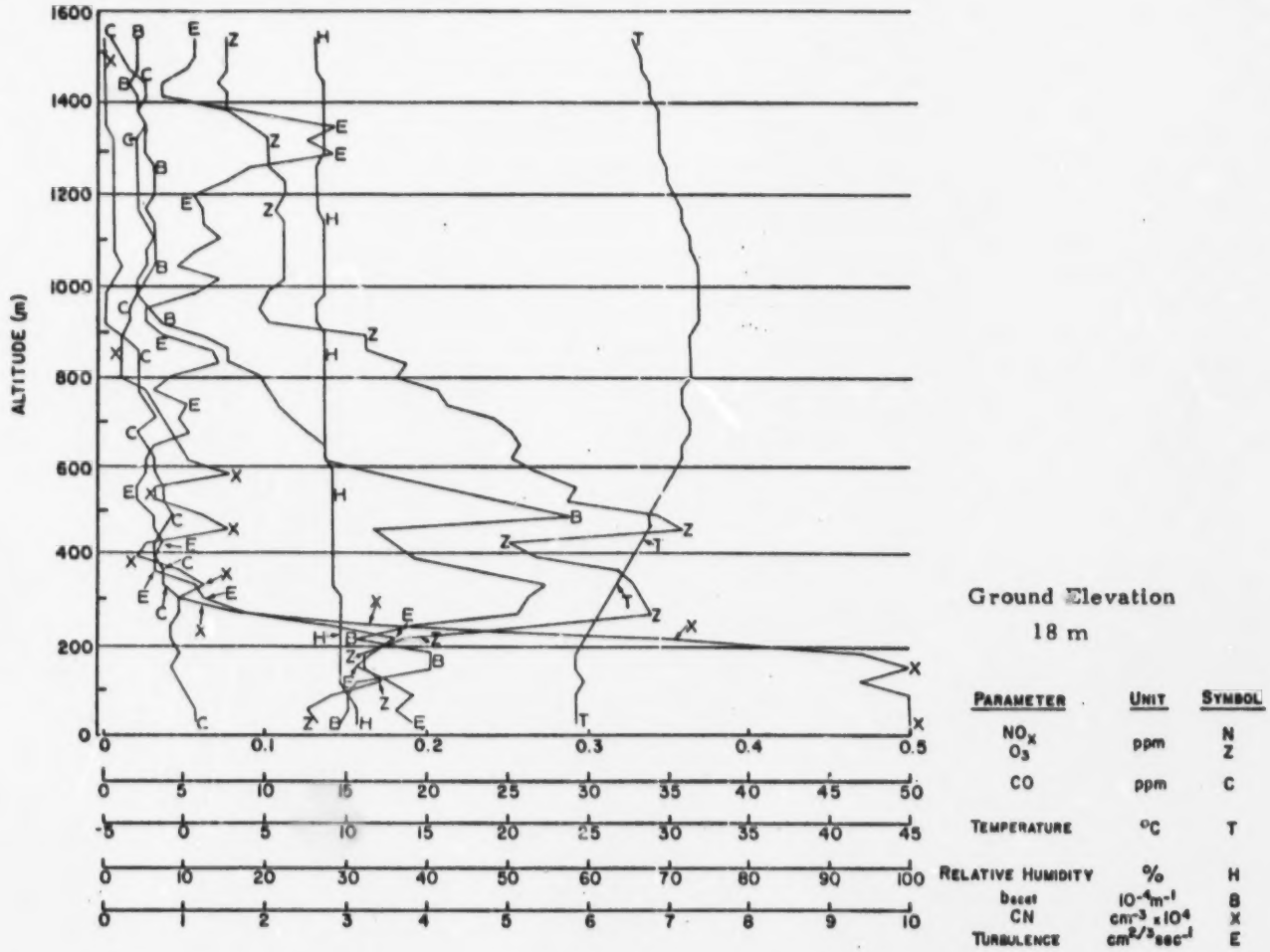

Fig. A-2. VERTICAL SOUNDING OVER HAWTHORNE (HHR)
JULY 25, 1973, 1106 PDT

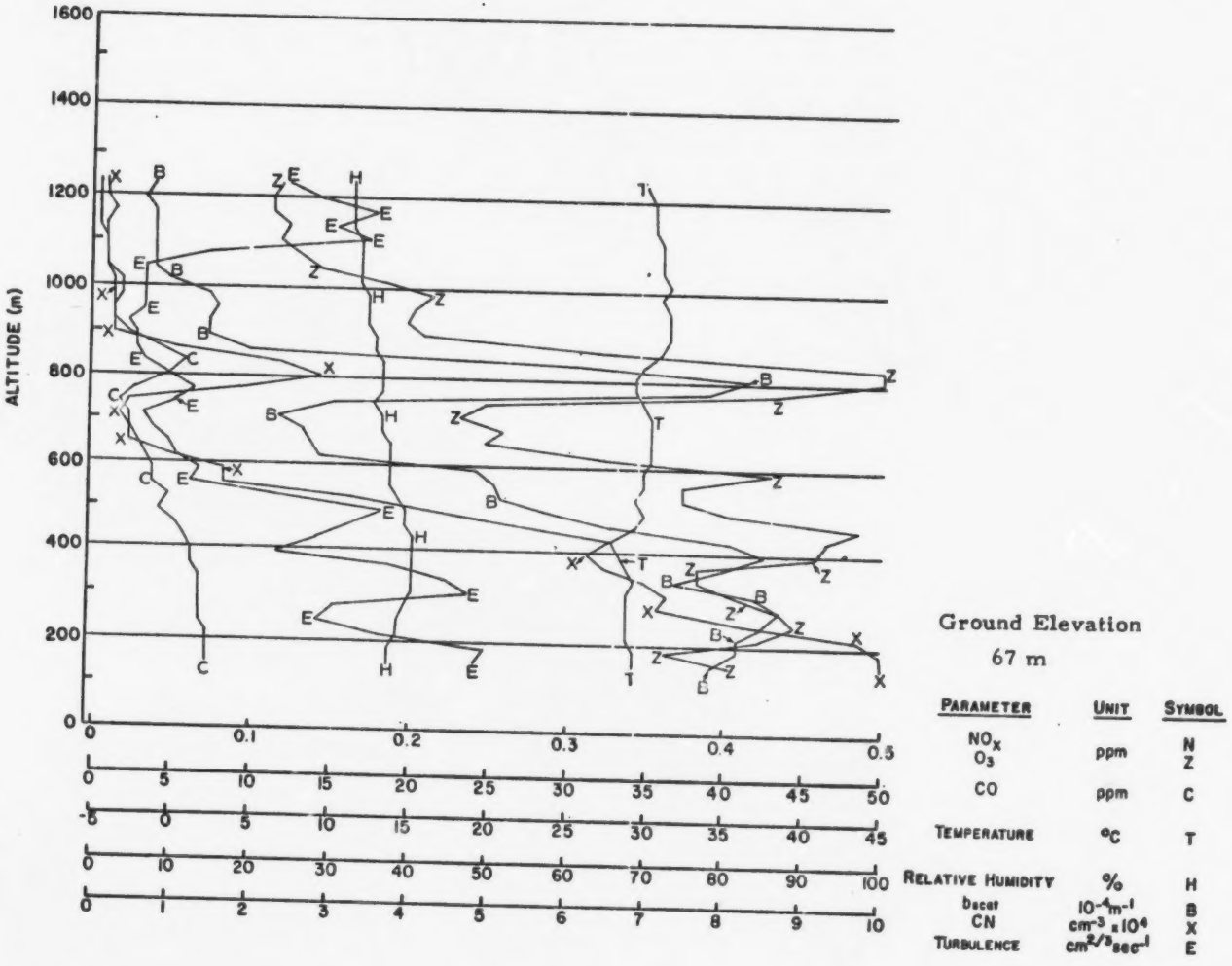

Fig. A-3. VERTICAL SOUNDING OVER SHEPHERD (SHE)
JULY 25, 1973, 1427 PDT

APPENDIX B

CHARACTERIZATION OF DENVER'S URBAN PLUME USING AN INSTRUMENTED AIRCRAFT

Characterization of Denver's Urban Plume Using an Instrumented Aircraft

by

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Paper No. 74-266

For presentation to the 67th Annual Meeting of the Air Pollution Control Association, Denver Convention Center, Denver, Colorado, June 9-13, 1974.

MRI 74 Pa-1173

Abstract

Paper No. 74-266

As part of an EPA coordinated air pollution study, an extensive three-dimensional air pollution mapping program was carried out in the Denver area during a 10-day period in mid-November, 1973. An aircraft instrumented to continuously measure scattering coefficient, condensation nuclei, O_3, NO_x, CO, SO_2, and flight parameters was used in the study. The aircraft was also equipped with instrumentation to measure the size distribution of grab samples.

The sampling pattern was designed to study the characteristics of the fresh pollutants in the morning drainage wind and those of aged pollutants in the plume later in the day. The urban plume was sampled during inversion conditions when it was trapped in a shallow mixing layer and also during periods of good mixing and ventilation.

The plume was found to be well defined and well mixed. High pollutant concentrations were observed aloft in power plant plumes which were subsequently ventilated to the ground as the mixing layer deepened. Photochemical processes were found to be important, and the ozone level in the plume was found to vary from 0.00 to 0.08 ppm. The background level outside the plume was always measured at between 0.03 and 0.05 ppm. The aerosol size distribution was also found to change character as the plume aged.

Introduction

Airborne measurements of gaseous and particulate pollutants as well as meteorological parameters affecting the pollutants were made with MRI's Cessna 205. The aircraft was flown during a ten-day portion of a major field experiment sponsored by the Environmental Protection Agency and undertaken in the Denver area during November 1973. Although a number of different agencies participated in the experiments, the purpose of this paper is to present selected airborne measurements and discuss these data in terms of their contribution to the understanding of urban plume produced by Denver, Colorado.

A major emphasis of the experiment was to study the physical and chemical characteristics of Denver's urban plume and the transport processes that affect the plume. In particular, the choice of both the airborne sampling paths and ground site locations were made to best study the aging processes that take place in the plume.

Previously, Riehl and Herkhof[1,2], Crow[3], and Riehl and Crow[4] have reported meteorological factors that affect air quality in the Denver area. We are unaware of any previous airborne measurements made on the Denver plume. Similar work, however, has been done in other areas such as St. Louis[5,6,7].

Description of the Program

The MRI aircraft as described by Blumenthal and Ensor[8] has been used extensively to measure the three-dimensional distribution of air pollutants. The sampling instrumentation used in the aircraft for the Denver study included fast time response monitors for O_3, NO_x, SO_2, CO, condensation nuclei, scattering coefficient, temperature, relative humidity, turbulence, altitude, and position. In addition, measurements of the size distribution of grab samples were made by installing a TSI Model 3030 electrical aerosol size analyzer in the plane. Liu et al.[9]

have described the use of such an instrument for the measurement of submicron aerosol size distributions. The size distributions were obtained in the aircraft by rapidly filling a large plastic bag (about 60 liters) to obtain the grab sample and then immediately analyzing the aerosol in the bag with the size analyzer.

Blumenthal[10] has described considerations for plume sampling as being dependent on the specific objectives of the particular study. One of the dominant meteorological factors in the Denver area is the drainage flow that normally exists during the morning hours. This flow carries the urban pollutant discharge northeast along the Platte river valley. Thus to optimize sampling, horizontal traverses and spirals were made at the points shown on Figure 1. Traverses at various altitudes were made along the routes marked I, II, or III and spirals were made at Standley Lake, Henderson, and near the EPA trailer location. Both the Henderson and EPA spiral locations were chosen because of ground measurements being made at these points and their close proximity to the expected plume centerline. The Standley Lake spiral was normally made to obtain useful background data. Unfortunately, sampling path II had to be terminated at Interstate 80S since flights over the Rocky Mountain Arsenal were prohibited.

Upper level wind data were obtained at both Arvada and the EPA trailer using pilot balloons (pibals). These data, as well as summaries of surface wind data, have been used in this paper and are based on information collected during the study and reported by Crow[11]. Other data used in this paper, including portions of the gas and b_{scat} data that were obtained at the EPA trailer and reported by Durham, et al[12], were also used to support the conclusions arrived at in this paper.

Experimental Results

Aircraft sampling was performed a total of six days in November 1973. Data from two of these days are presented here to illustrate various urban plume phenomena.

November 20 - Urban Plume Structure

November 20 represents an excellent reference point to begin an air pollution episode. A snowstorm invaded the Denver area in the afternoon of the 19th and lasted until the early morning hours of the 20th. Surface winds for the 20th were generally from the south throughout the day, and thus the plume consisted of fresh pollutants which aged as they traveled northward. The freshly cleaned air mass outside the plume and the relatively constant net flow produced an almost ideal sampling situation and a plume with a fairly simple structure. Figure 2 indicates the streamlines at 11:00 a.m. as well as an outline of the urban plume as determined by horizontal traverses and photographs.

Figure 3 shows a cross section of the plume obtained at 6200 ft msl along sampling route II (see Figure 1) from Highway 287 to Highway 805 at about 10:00 a.m. A distinct increase in NO_x, CO, and scattering coefficient at approximately the 1.5 mile point indicates the western edge of the urban plume. A further increase in NO_x, SO_2, and scattering coefficient and a slight decrease in ozone at the 4.5 mile point probably indicate penetration of the bottom edge of the Cherokee power plant plume. The decrease on O_3 is due to scavenging of ozone by freshly emitted NO.

Figure 4 is a vertical profile taken near the EPA trailer at 10:55, an hour after the cross section in Figure 3. The temperature profile indicates a slightly stable lapse rate with a weak inversion starting at 6400 ft msl (about 1200 ft above ground). Up to about 5800 ft msl, the

various pollutants are well mixed and occur in about the same concentrations as were seen throughout the urban plume cross section shown in Figure 2. Between 5900 ft and 6600 ft msl, however, the power plant plume is superimposed on the urban plume in a distinct, well defined layer, the power plant plume being confined by the weak inversion layer.

Characteristics of the power plant plume include high levels of primary pollutants such as NO_x, SO_2, and particulates and a very low level of ozone due to scavenging by NO. This type of layer aloft containing high concentrations of pollutants (in this case $NO_x > 0.5$ ppm) can persist for long periods of time and can be transported many miles before being ventilated to the ground when finally entrained by a deepening mixing layer.

Above the inversion at about 6700 ft msl, the pollutant levels drop off to virtually clean air values. Note however that the ozone level is approximately 0.04 ppm. This level has been observed in many areas of North America in very clean air and often represents the ozone background level[13]. In the urban plume below the power plant plume, the ozone level is considerably higher than the background level indicating photochemical production of ozone.

Figure 5 is a vertical profile taken in the urban plume at Henderson shortly before the one in Figure 4. Since the power plant plume seen in Figure 4 was not directly over Henderson at this time, no indication of it is seen in the profile. The temperature profile at Henderson indicates a slightly stable lapse rate with a weak inversion beginning at 6200 ft msl, about 200 ft lower than the one at the EPA trailer. The higher inversion level at the EPA trailer may be an indication of the urban heat island effect.

The pollutant levels measured in the urban plume at Henderson are similar to those presented earlier and indicate a plume which is well mixed both horizontally and vertically. The plume at Henderson is fairly

uniform in concentration up to a level of about 5900 ft where mixing is impeded and concentrations start to drop off, reaching clean air values near 6400 ft.

Figure 6 is a vertical profile of the urban plume over the EPA trailer at about 2:00 p.m. The wind is still from the south. Due to surface heating, the mixing layer has deepened, yet pollutants are still confined to a layer about 2000 ft thick. The power plant plume is no longer well defined on this or other afternoon traverses and has evidently been entrained in the surface mixing layer. Integration throughout the mixing layer shows that the total pollutant budget is clearly higher than during the morning flight reflecting the entrainment of the power plant plume and the overall accumulation of pollutants during the day. It is interesting to note that photochemical processes are active, even at temperatures of 0°C and that the ozone level in the mixing layer is approximately equal to the ambient air standard of 0.08 ppm.

The data from November 20 verify several statements made by Riehl and Herkhof [2]. In a discussion of turbulent transport, they surmise that "during daytime, the polluted layer must extend well above 100 m with characteristics almost those of a mixed layer." Figures 4, 5, and 6 indicate that, at least on November 20, the polluted layer was well mixed during the day and extended up to about 900 ft (or 300 m) in the morning and to 2000 ft (or 650 m) by midafternoon. Similar characteristics were also observed on other days. In addition, they conclude that "non-persistence of a temperature inversion through the noon hours is not a good guide for current and subsequent air pollution levels." Figures 5 and 6 indicate the problem associated with using the inversion level to predict the depth of the mixed layer and thus to some extent the surface concentrations. Using the inversion level in Figure 5 as a guide to mixing depth would lead to an assumed mixing layer height of 6200 to 6400 ft msl or 1000 to

1200 ft above ground level. Using the actual pollutant concentrations as an indicator of mixing layer height leads to an actual mixing depth of only 600 to 800 ft. In Figure 6, no significant inversion is indicated, yet the pollutants are reasonably well confined to a layer about 2000 ft deep.

November 21 - Pollutant Characteristics in the Urban Plume

November 21 represents the second day of an episode which began during the morning hours of November 20. During the late afternoon and evening of November 20, winds were light and variable and a strong radiation inversion developed. Thus, pollutant levels increased over the city. The morning of November 21 was clear with light surface winds from the south producing streamlines similar to those shown in Figure 2. By late morning, the wind field had started to shift to an easterly flow, and shortly after noon the wind speed increased abruptly to a strong flow from the east, moving the pollutants up against the foothills to the west of Denver.

Figure 7 is a vertical profile taken at 0925 MST near the EPA trailer site, and Figure 8 is another profile taken at the same location at 1242 MST. Figure 7 shows a dense polluted urban plume trapped beneath a strong radiation inversion with clean air above the mixing layer. At this time, photochemical production of ozone within the mixing layer had not yet exceeded the scavenging of ozone by freshly emitted NO or by NO which had accumulated overnight. The ozone level in the mixing layer was thus depressed from the clean air level above.

Figures 9 and 10 illustrate in more detail the character of the urban plume during the morning. The figures show aerosol size distributions obtained at the low point of the spirals shown in Figures 7 and 8, respectively. Both surface and volume distributions are plotted.

Whitby and his associates[14,15] have shown that combustion sources generate fresh aerosol in the size range under 0.1μm diameter. However, as the aerosol ages and photochemical generation of new aerosol material occurs, the size distribution will shift, and the aerosol will coagulate and accumulate in the 0.1-1μm diameter size range. This process is accelerated if the fresh combustion aerosol is emitted into a background of aged polluted air already containing large amounts of particulates in the 0.1-1μm size range.

The surface distribution shown in Figure 9 includes both a large peak at 0.4μm diameter (called the "accumulation mode" by Whitby) and a smaller inflection in the distribution at 0.04μm diameter. This indicates that the morning urban plume at this location consists of a mixture of well-aged pollutants accumulated over night plus freshly emitted effluents.

By the time the 1242 MST sounding (Figure 8) near the EPA trailer was made, the wind shift mentioned earlier had occurred. Cleaner, rural air had replaced the urban plume existing at this location earlier in the day (0925 MST, see Figure 7). In Figure 8, the ozone level is at a clean air value, other pollutant levels are quite low, and the temperature inversion has disappeared. The surface area distribution shown in Figure 10 indicates a small amount of fresh combustion aerosol from an unidentified source nearby, but no large "accumulation" mode is present.

Figure 11 is a profile taken over Standley Lake at 1134. This profile shows the change in character of the urban plume as it ages. The air in the mixing layer had probably traveled north from Denver and then moved westward with the wind shift. It had thus had a chance to age for a few hours since passing over a concentrated source area. The profile was taken before the abrupt increase in wind speed and an inversion layer is still present. The mixing layer has deepened since the morning sounding due to surface heating, but the plume is still confined within a layer about 1000 feet deep.

Primary pollutants such as CO, SO_2, and NO_x have remained at relatively high values; but ozone, a secondary pollutant, has now increased above the clean air value, equaling the Federal ambient air standard of 0.08 ppm in places. Figure 12 is a size distribution obtained at the bottom of the spiral shown in Figure 11. A well-developed "accumulation" mode is seen with little evidence of fresh combution aerosol.

Thus, as the urban plume ages in the absence of fresh emissions and in the presence of sunlight, the aerosol size distribution shifts to the "accumulation" mode, the rate of production of ozone surpasses the rate of scavenging, and the ozone level increases. Although it was not measured independently by the aircraft, the EPA van data show that, as the plume ages, the NO_x shifts from being mostly NO to mostly NO_2. This is consistent with the increase in the ozone level.

Riehl and Herkhof[a] in their studies had assumed that aerosol mass was a good indicator of the source strength of the city and that it was a conservative quantity. It is evident from our results that photochemical processes occur in the Denver area, and that the size distribution in the plume changes with time. One must use caution when assuming that aerosol mass or other aerosol parameters are conservative quantities since photochemical production of aerosol is a definite possibility.

Conclusions

1. Under the conditions measured, Denver was shown to have a well-developed and well-mixed urban plume which varied in thickness from 500 to 2000 feet depending on the stability and the amount of surface heating. The temperature lapse rate, however, was not always a good indicator of mixing depth.

2. Large buoyant stationary source plumes generate layers aloft which are ventilated to the surface when the mixing layer deepens.

These plumes are characterized by high levels of primary pollutants and a deficit of ozone relative to the surrounding air.

3. The chemical and physical characteristics of the urban plume constituents change as the plume ages. In the presence of NO sources and in the absence of photochemistry, ozone is scavenged; but when sunlight is present, photochemistry is important, and ozone levels in the urban plume can reach or exceed the Federal ambient air standards. Photochemical production of aerosol may also occur in the plume.

4. The aerosol size distribution changes shape as the plume ages, and the submicron aerosol accumulates in the 0.1 to 1 μm diameter size range.

5. The ozone level in clean air outside the urban plume was measured at 0.03 to 0.05 ppm on all flights, while the level in the plume varied from 0.00 to 0.08 ppm depending on the level of photochemical activity and the amount of scavenging by other pollutants.

Acknowledgments

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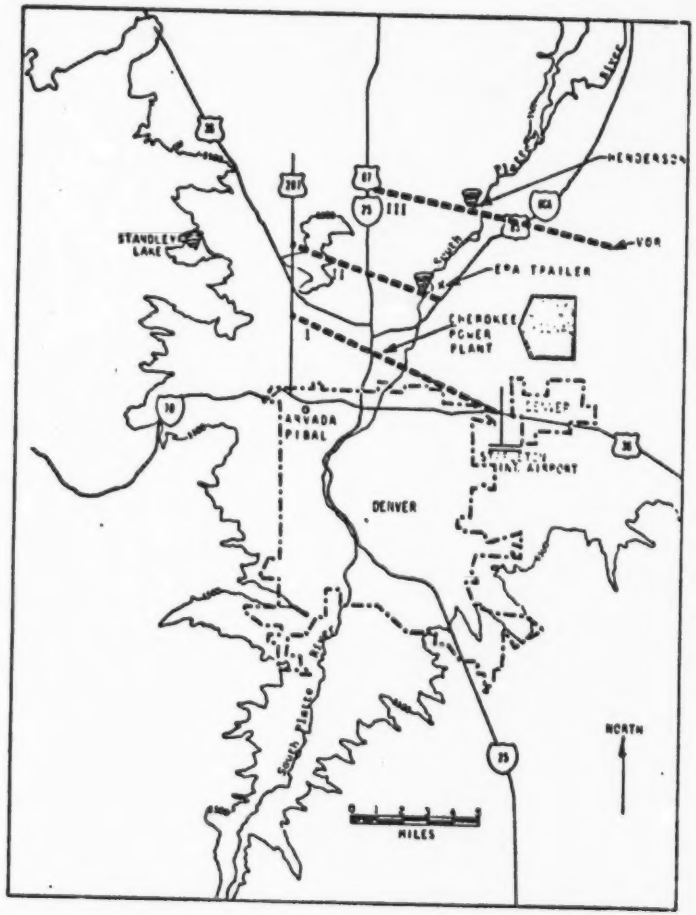

Figure 1. Denver and the surrounding area. Sampling paths and spiral locations are shown.

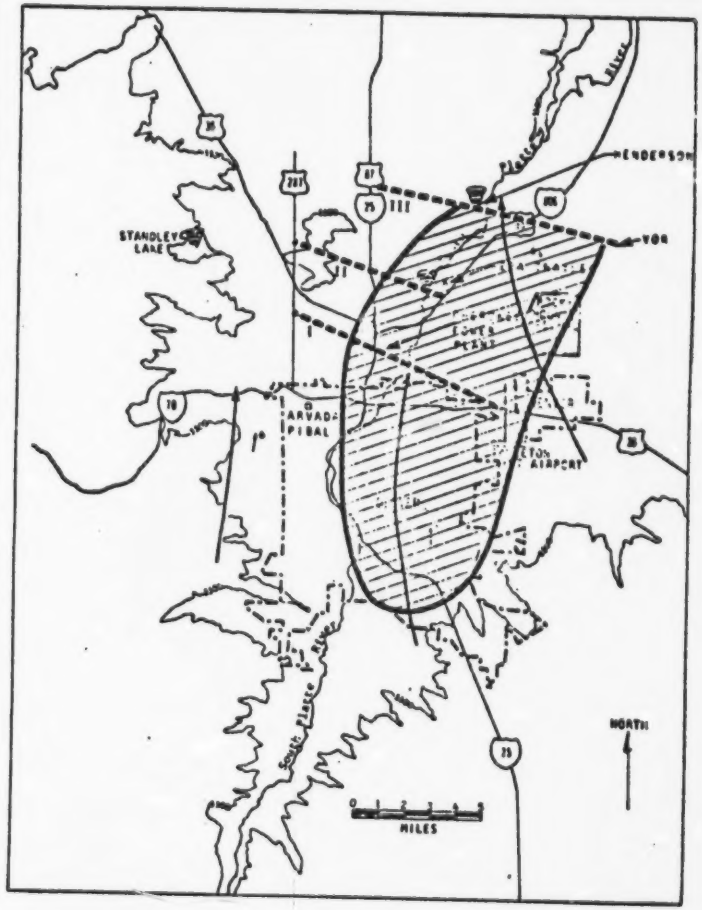

Figure 2. Streamline analyses and location of urban plume. November 20, 1973, 1100 MST.

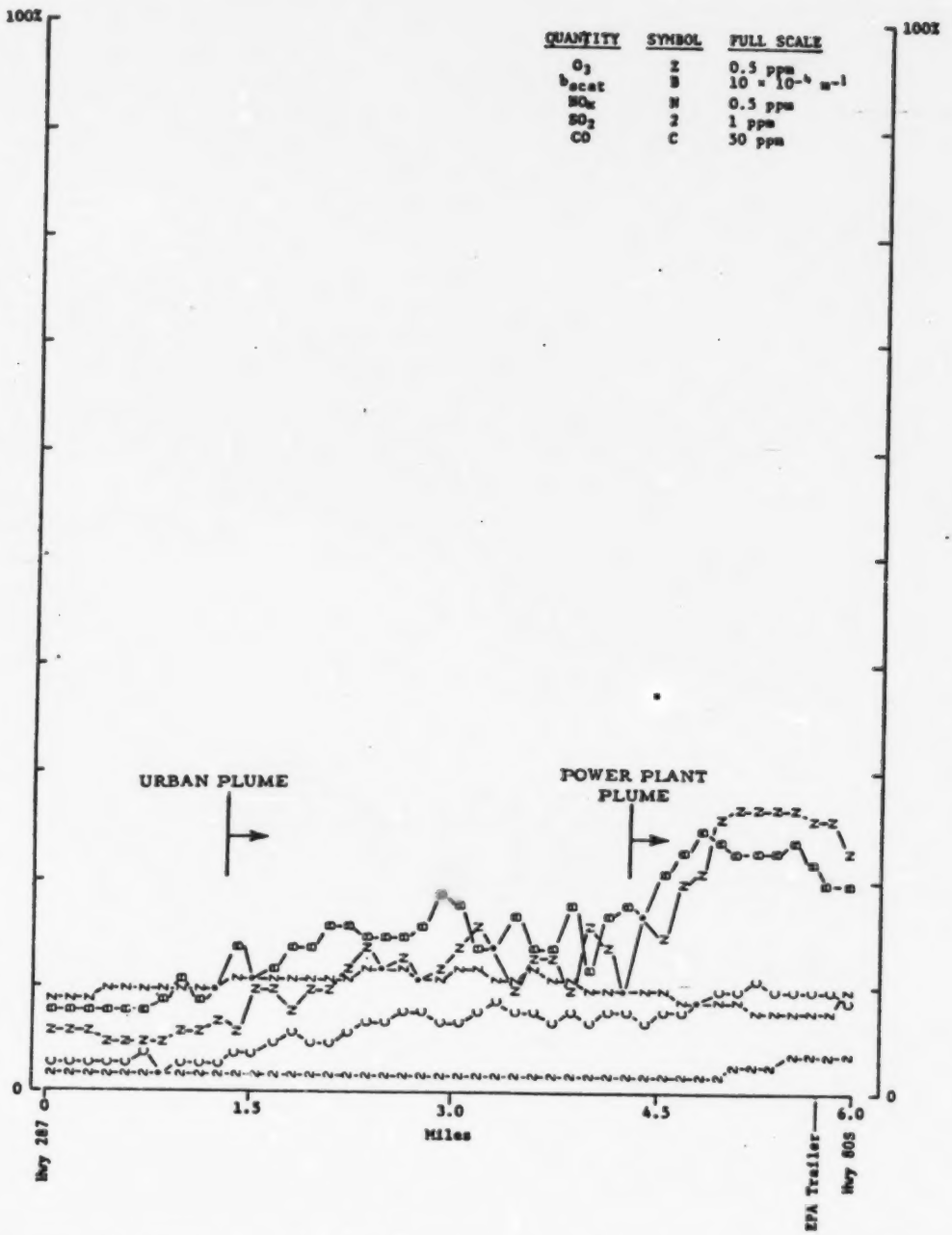

Figure 3. Cross section of Denver urban plume at 6200 ft msl along Sampling Route II. November 20, 1973, 1000 MST.

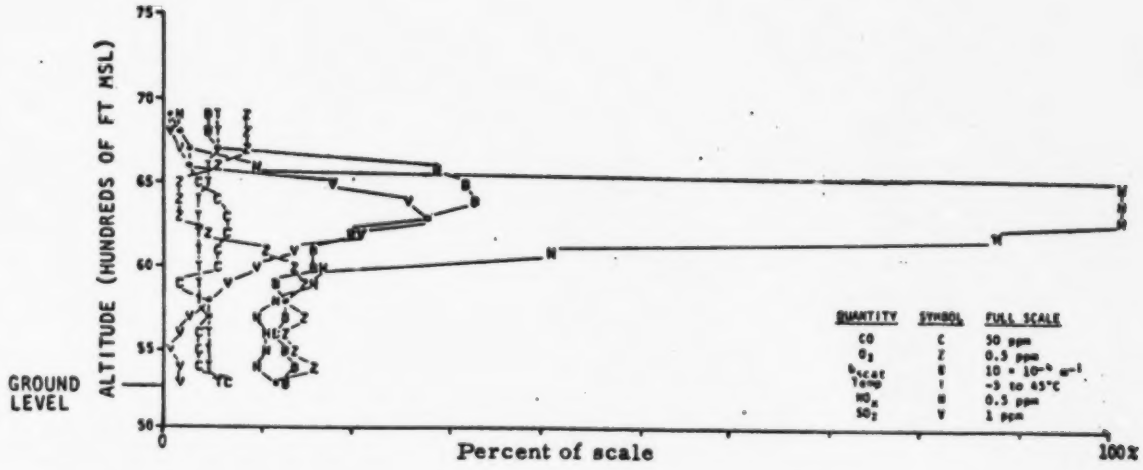

Figure 4. Vertical profile near the EPA trailer. November 20, 1973, 1055 MST.

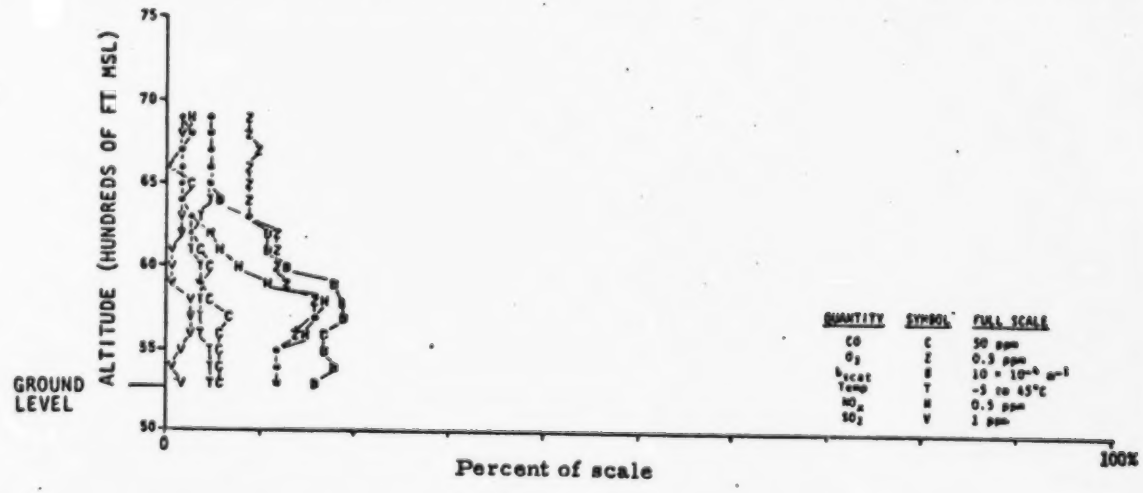

Figure 5. Vertical profile at Henderson. November 20, 1973, 1047 MST.

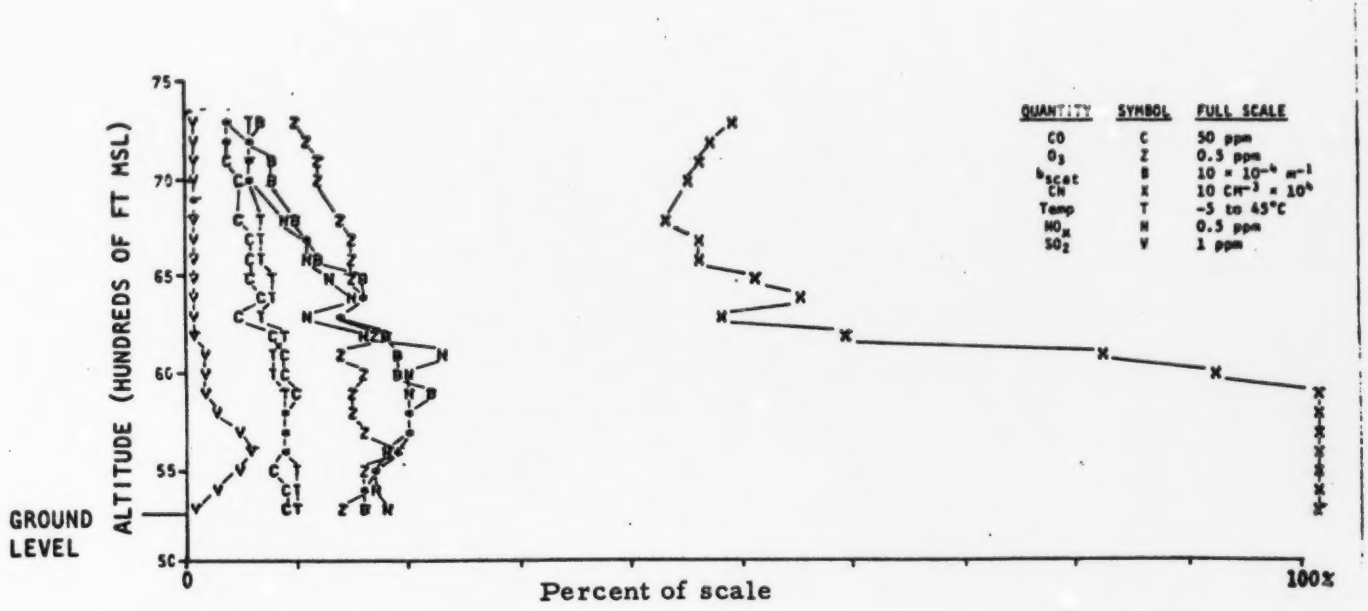

Figure 6. Vertical profile near the EPA trailer. November 20, 1973, 1400 MST.

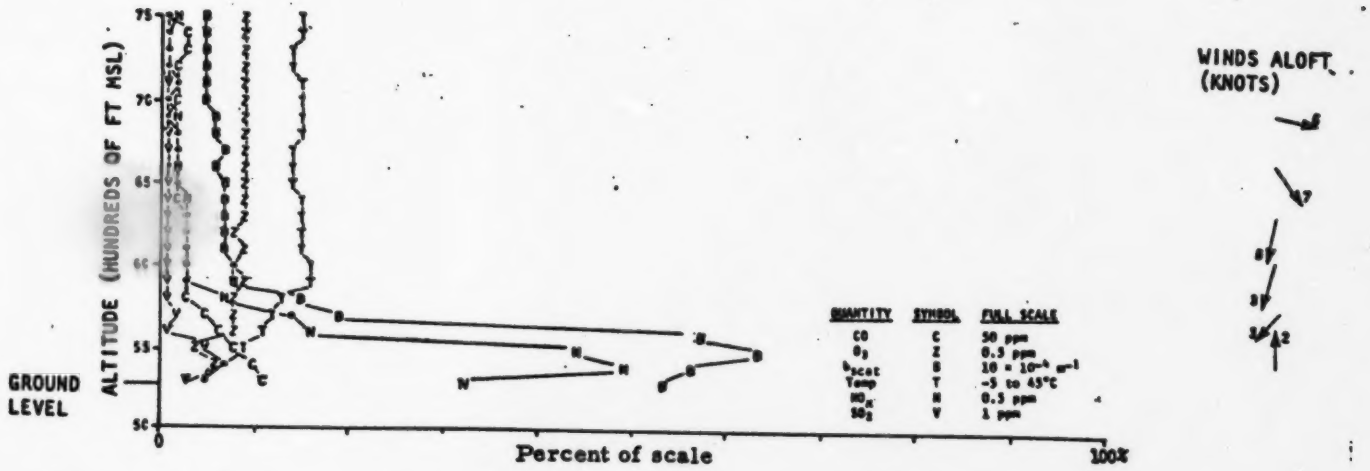

Figure 7. Vertical profile near the EPA trailer. November 21, 1973, 0925 MST

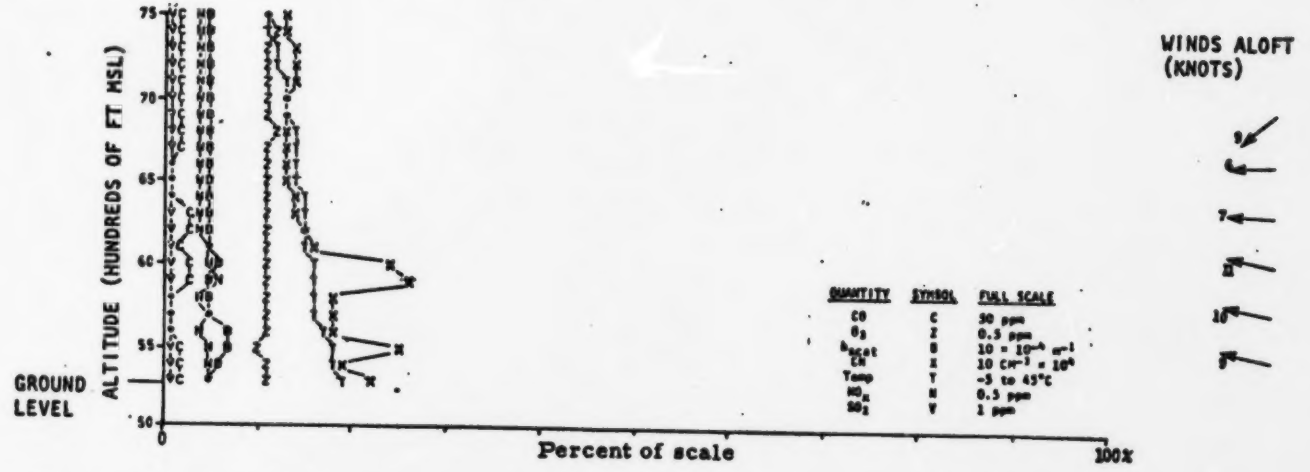

Figure 8. Vertical profile near the EPA trailer. November 21, 1973, 1242 MST

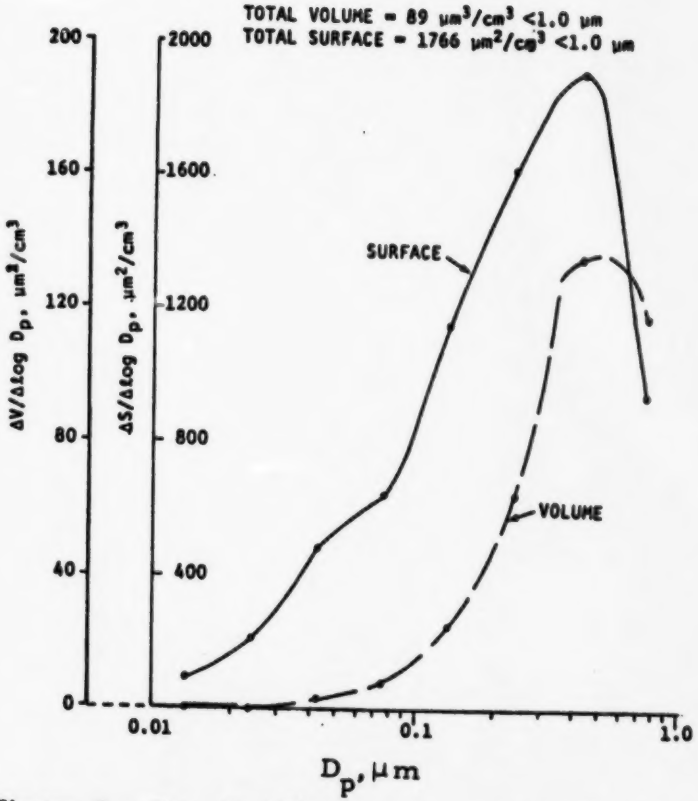

Figure 9. Size distribution of aerosol obtained at lowest point of spiral near EPA trailer (see Figure 7). November 21, 1973, 0925 MST.

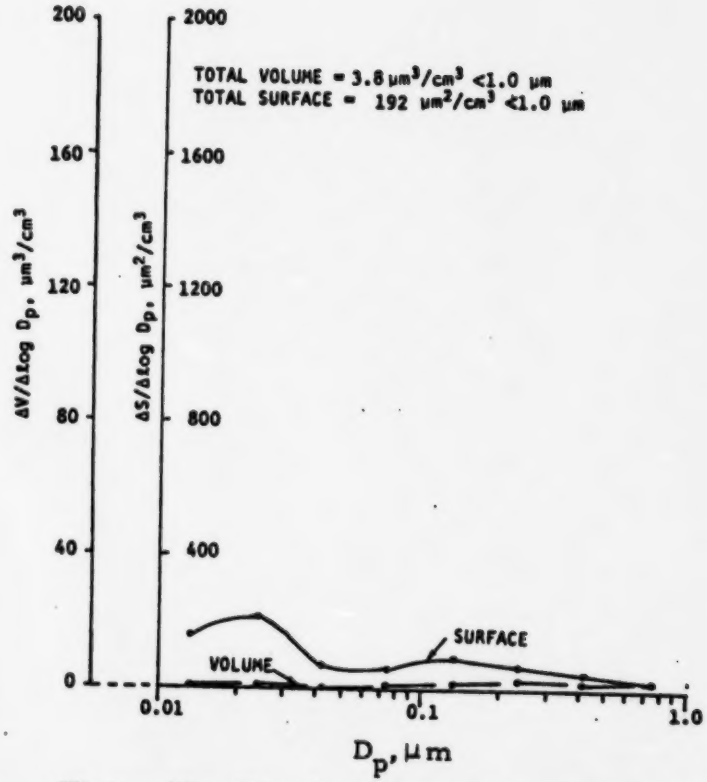

Figure 10. Size distribution of aerosol obtained at lowest point of spiral near EPA trailer (see Figure 8). November 21, 1973, 1242 MST.